Journal of Hazardous Materials 490 (2025) 137841

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Quantification of microplastics in agricultural soils by total organic carbon -solid sample combustion analysis

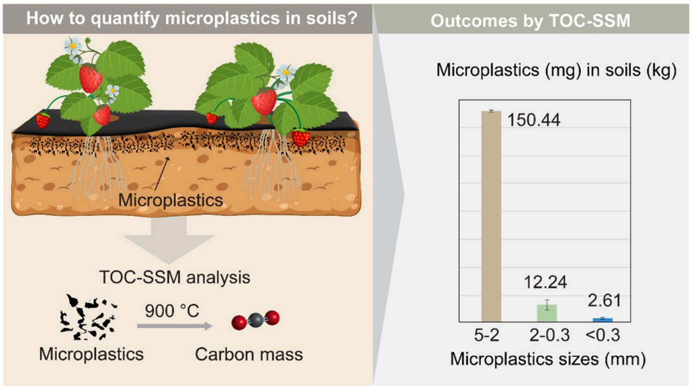
Yoonjung Seo [a,*], Yunru Lai [b], Guangnan Chen [a], John Dearnaley [a], Shaobin Wang [c,*], Xiaohuan Liu [d], Pingan Song [a,e,**]

[a] *School of Agriculture and Environmental Science, University of Southern Queensland, Toowoomba, QLD 4350, Australia*
[b] *Centre for Sustainable Agricultural Systems, University of Southern Queensland, Springfield, QLD 4300, Australia*
[c] *School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia*
[d] *College of Life Science, Zhejiang Provincial Key Laboratory of Plant Evolutionary Ecology and Conservation, Taizhou University, Taizhou 31800, China*
[e] *Centre for Future Materials, University of Southern Queensland, Springfield, QLD 4300, Australia*

HIGHLIGHTS

- TOC-SSM can effectively quantify microplastic (MP) mass in soils.
- Organic matter removal is crucial for accurate TOC-SSM microplastics analysis.
- Black polyethylene was the dominant plastic residue in strawberry fields.
- Decreased MP size correlated with lower MP contamination by mass.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Microplastic quantification
Microplastic mass
Microplastic contamination
Agricultural soil
Mulch films

ABSTRACT

Accurate quantification of microplastics (MPs) in soils is a significant challenge due to the complex nature of the organo-mineral matrix. Fine mineral particles and organic matter often interfere with the efficiency of extraction, identification and quantification of MPs from soils. Here, an optimized MP extraction and quantification method is proposed, using total organic carbon analyser-solid sample combustion unit (TOC-SSM) analysis. The approach entails a field survey, digestion of organic matter by Piranha solution, density separation, and quantification. This method achieves a high total recovery rate of 97.39 ± 14.25 (SE) % for particles sized between 300 and 600 μm, and 94.80 ± 13.48 (SE) % for particles less than 300 μm with spiked soil as samples. The optimised method is then applied to strawberry farm soils that use plastic mulch films to quantify MP contamination levels. Our results indicate MP concentrations of 12.24 ± 3.65 (SE) mg kg^{-1} (for particles of 300–2000 μm in size) and 2.62 ± 0.66 (SE) mg kg^{-1} (for particles smaller than 300 μm). With improved simplicity and the ability to

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* Corresponding authors.
** Corresponding author at: School of Agriculture and Environmental Science, University of Southern Queensland, Toowoomba, QLD 4350, Australia.
E-mail addresses: Lenny.Seo@usq.edu.au (Y. Seo), shaobin.wang@adelaide.edu.au (S. Wang), Pingan.song@usq.edu.au, pingansong@gmail.com (P. Song).

https://doi.org/10.1016/j.jhazmat.2025.137841
Received 26 November 2024; Received in revised form 24 February 2025; Accepted 2 March 2025

provide the actual weight of plastics for the extraction and quantification of MPs, this work offers a potential approach for assessing low-density plastics in the northeastern Australian agricultural soils with a dominant MP contamination, specifically polyethylene (PE).

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1. Introduction

Agricultural soils receive plastic residues and microplastics (MPs) via various pathways such as the application of biosolids, the use of plastic mulch films and other plastic products [37]. Polyethylene (PE)-derived MPs are major plastic residues in the agricultural industry and biosolids in Australia [27].

The potential impacts of MPs on the environment are profound and multifaceted. Due to their persistence, plastics do not degrade easily in the environment. Instead, they often accumulate in various ecosystems, leading to numerous environmental challenges. In soils, MPs can alter soil physical properties, leading to negative impacts on soil structure, bulk density and soil-water dynamics [5]. Chemically, MPs interact with soil pH, electrical conductivity (EC) and cation exchange capacity (CEC), while also releasing chemicals into surrounding soils [37]. These multi-impact influence soil microbial communities and enzyme activities, potentially disrupting soil fertility and ecosystem functions [44]. When these issues arise in agricultural soils, plants may be impacted directly or indirectly. Altered soil conditions could potentially impact plant growth, crop yield and quality [40]. Various types of MPs can negatively impact plant growth, inducing growth inhibition, root damage, oxidative stress, and altered element uptake [41]. While certain types of MPs may promote plant biomass growth, they can also negatively affect soil aggregation and microbial activity, leading to complex long-term consequences on both soil properties and crop performance, ultimately impacting overall agricultural productivity and biodiversity [21,35]. Food safety is a growing concern, as the ingestion of MPs into the human body poses potential risks [37]. MPs have been found in various fruits and vegetables [28], and direct uptake of MPs from hydroponics has been reported in lettuce study [16], raising further concerns about the transfer of MPs into the human food chain.

Prevention of contamination is one key requirement for a sustainable agroecosystem. Mitigation or remediation processes often incur a high cost and might not be feasible to solve the contamination issue [37]. Thus, monitoring contaminants and establishing proper actions before contamination occurs is particularly important. Quantitative and qualitative measurements of contaminants are the essential steps for monitoring and risk assessments. Without proper quantification, it is not possible to establish reliable data and allow effective risk prediction and management. MPs are emerging contaminants and their quantification in soils is particularly challenging due to the heterogeneity of soil and MP characteristics [37].

In previous studies, MPs were usually quantified by the number of particles or items per soil mass (kg) [31–33]. These units are only useful when particle type, size, shape, thickness and density are uniform, or when the aim is to assess the variability in these characteristics. However, each plastic product has unique properties, and even the same products can have different colours, thicknesses and additives by the manufacturers [23]. Moreover, aged plastics in the field may have altered properties induced by sunlight, dry-wet cycle and organic matter. Thus, the expression in particles or item numbers is not adequate to understand MP behaviour in soils. One of the more appropriate options for quantifying MPs is plastic mass per soil mass. Larger particles (i.e., > 2000 μm) may be quantified by simply weighing them after cleaning and separation while smaller particles can only be counted or estimated by shape and density for quantification.

Mass quantification has been attempted with specialized equipment such as thermal extraction and -desorption-gas chromatography/mass spectrometry (TED-GC-MS) and pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) [20,26,4,7]. However, the approaches cannot determine particle sizes and shapes. When soil samples contain a high amount of organic matter, the sample needs to be digested before the analysis [18,22]. The TED GC-MS and Py-GC-MS are powerful techniques, highly accurate for localized and precise measurement of MP contamination (ng g^{-1}), making them ideal for detailed analysis of small sample sizes [18]. However, these methods may not provide a comprehensive representation of broader contamination levels. A small size of the whole sample may not accurately represent the actual concentration of MPs since MPs are often not evenly distributed in soils. A larger sample size, typically in the range of several grams or more, is better suited to reflect MP contamination more effectively across soils. Particularly, PE is difficult to measure precisely by these methods as it has a similar degradation temperature to organic matter in TED-GC-MS [7] and exhibits a large variety of signature compounds but a low area ratio of pyrolysis products in Py-GC-MS [20]. Therefore, these approaches often require chemical digestion or pre-treatment steps to increase sensitivity and reduce matrix interference [8]. Furthermore, the Py-GC-MS can only provide pure polymer mass [29]. Determining the actual product mass is crucial for assessing the harmful impacts of MPs, as plasticisers and additives in MPs are the primary components responsible for those adverse effects [9].

While Py-GC-MS quantifies polymers by identifying signature compounds, the total organic carbon analyser-solid sample combustion unit (TOC-SSM) quantifies materials by measuring their carbon content. It completely combusts the material to convert its carbon into carbon dioxide, which is then detected to calculate the absolute carbon mass. TOC-SSM demonstrated its ability to accurately calculate carbon content in pure polymers with over 95 % accuracy [11]. Although there have been no studies using TOC-SSM for analysing MPs, TOC-L has been successfully applied to quantify MPs in liquid samples from sewage sludge after filtration [14]. A key difference between TOC-L and TOC-SSM is that the injection needle in TOC-L restricts particle size due to the risk of clogging, whereas TOC-SSM does not have such size limitations, allowing for the analysis of a broader range of particle sizes, including those in the 100–2000 μm range. MPs in a particle size range of 100–2000 μm are prevalent in environmental samples. Considering the limitations of optical sorting and thermoanalytical equipment, the TOC-SSM method provides a robust, scalable approach for accurately quantifying MPs within this range. Unlike other methods that face challenges with large particle sizes or small sample sizes, TOC-SSM's ability to process larger sample sizes without limitations on particle size offers a promising solution for overcoming obstacles in MP extraction and quantification in soils.

Accurate assessment of MP contamination in agricultural soils requires robust methodologies and universally applicable analytical tools, as these contribute to a more precise understanding of MP contamination and facilitate the development of regulatory frameworks. A key challenge in MP analysis lies in achieving high accuracy and reproducibility in extraction and quantification methods, which typically include density separation, digestion of organic matter, optical sorting and specialized equipment such as Py-GC-MS. This study aims to address the gap by developing a highly reproducible method for MP quantification in the northeastern Australian agricultural soils, focusing on PE contamination. The outcomes are expected to provide valuable insight into MP contamination levels in agricultural soil, particularly those exposed to PE mulch films, and contribute to the broader effort of establishing reliable MP quantification methods in environmental research.

2. Experimental design

This study aimed to test different combinations of density separation and digestion of organic matter to find optimum extraction methods for the northeastern Australian agricultural soils. Experiments were set up to evaluate the efficiency of MP quantification after the extraction from soils by a combination of digestion and density separation procedures (Fig. 1). Further, TOC-SSM was measured to quantify MPs from soils. TOC-SSM is relatively simple to operate and provides straightforward results to calculate MP weight. We also illustrate the developed method application using a case study of soils from a strawberry farm.

2.1. Reference MP preparation

Microplastics used in reference soils for method validation were obtained by milling (i.e., 15 seconds three times in a coffee grinder) commercially available materials followed by sieving using 300 and 600 μm pore-sized metal sieves. PE-MPs were prepared from irrigation hoses collected from the field (donated by a recycling company, Australia Sunlight Group Pty Ltd). Non-milled and milled materials were compared through the attenuated total reflectance - fourier transform infrared spectroscopy (ATR-FTIR, Shimadzu, Japan) to observe any chemical alteration or degradation by mechanical milling.

The physical characteristics of the obtained MPs were observed by a stereomicroscope (Olympus, SZ61) and scanning electron microscopy (SEM, JEOL, JCM 6000) before spiking them into soil samples. The shape of MP fragments was observed using a stereomicroscope with an Olympus DP23 camera at 20 × magnification and PRECiV Core software package. The surface of the produced MPs was observed by SEM at an accelerating voltage of 5 kV with gold coating.

2.2. Reference soil sampling and MP spiking

Reference soils were collected from the University of Southern Queensland, Toowoomba campus (P block). The selected sampling site had no prior history of plastic mulch film application and was characterized as a sandy clay loam based on its particle size distribution (53.08 % sand, 20.92 % silt, and 26 % clay). To assess the chemical properties of the soil, the pH (5.5) and electrical conductivity (EC, 0.05 dS m^{-1}) were measured in a 1:5 soil-to-water suspension at 25 °C. Samples were collected in random locations and combined to make composite samples. At least 10 random points in the depth of 0–20 cm were chosen for one composite sample. Soil samples were collected by a manual soil auger (diameter 75 mm) and thoroughly mixed for one composite sample (total of around 2 kg). Although the sampling site did not use plastic mulch film, they may have MPs by air deposition or other pathways of contamination.

The collected soil samples were air-dried and sieved through 2 mm

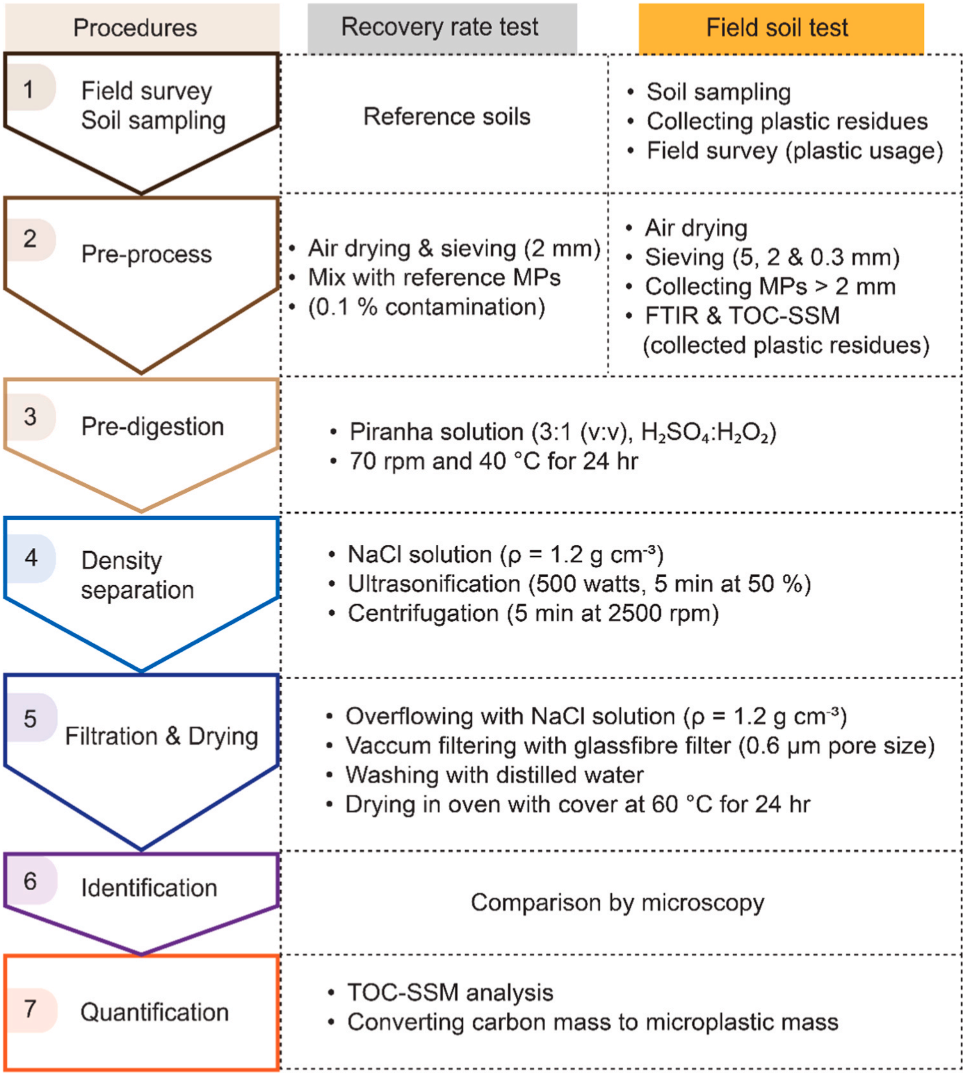

Fig. 1. Flow chart of extraction protocol optimized for polyethylene-microplastics.

mesh for spike-recovery experiments. We used metal trays for drying to avoid any potential secondary plastic contaminations, and drying was conducted at room temperature for 48 hours after gently crushing soil samples. High temperature drying could potentially lead to degradation and alteration of MPs in soils. Sieving was conducted using a metal sieve with a pore size of 2 mm [34]. Prepared reference PE-MPs were added to soils in a glass beaker and mixed with a glass rod for 1 min to achieve a concentration of 0.1 % by weight (w/w), with 30 mg MPs in 30 g of spiked soil.

2.3. Digestion of organic matter

We tested three different digestion methods used in previous studies: Fenton's reagent (H_2O_2 with Fe(II)SO_4; 4:1) at 60 °C; H_2SO_4 with H_2O_2 (1:40) at 60 °C; and Piranha solution (H_2SO_4 with H_2O_2; 3:1) (W. [17,36,42]). Briefly, 5 g of MP spiked soil sample was placed in a beaker. The beaker was merged into an ice-water bath and around 4 mL of 0.05 M Fe(II)$SO_4 \cdot 7\ H_2O$ solution and 10 mL of 30 % H_2O_2 solution were added to the soil sample in increments. The flask was placed under a fume hood for five minutes or more until it had a stable temperature. Once the reaction settled, 10 mL of 30 % H_2O_2 solution was added again. The flask was left in an orbit shaker at 70 rpm and 60 °C for 24 h. Digestions with H_2SO_4 with H_2O_2 (0.5:20 mL) at 60 °C and Piranha solution at 40 °C were carried out using similar steps. The digestion methods were compared based on the simplicity of procedures (whether requiring additional steps) and efficiency in cleaning the surface of MPs (minimizing potential errors in mass quantification). Each digestion solution was evaluated by measuring the removal of total carbon content in soil samples using TOC-SSM, and surface cleanliness was assessed through microscopy.

The preferred solution, Piranha solution (as described in Section 3.2), was further investigated for potential alteration to the PE via ATR-FTIR and its digestion efficiency using samples from three farms without any known history of plastic mulch film usage and biosolid application (Table 1). The soil samples used in this study were collected from various locations in Queensland and New South Wales, representing a range of clay-rich soil types found in northeastern Australian agricultural systems (e.g., Vertosols, Dermosols, and Ferrosols). A total of 10 composite soil samples (ID from S1 to S10) were collected in random spots with a 40 mm internal diameter soil core tube with a Honda-Christie post-hole rammer. Cores were taken to a depth of 100 cm and segmented into different sample depths. The 0–10 cm samples were retained for analysis for our study.

2.4. Density separation

After the digestion of organic matter, density separation was performed to separate soil minerals and MPs. $ZnCl_2$, NaBr and NaCl solutions were tested for the density separation. $ZnCl_2$ and NaBr solutions were prepared by dissolving 1000 g of salts in 550 mL of distilled water and then diluted to 1000 mL at a density of 1.6 g cm^{-3} at room temperature. NaCl solution was prepared by similar steps, and the final density was 1.2 g cm^{-3} at room temperature.

The digested mixture was added to around 150 mL of the preferred solution and dispersed by the ultrasonifier (Vibra-Cell™, VCX-500–220) at amplitude 50 % for 5 min and then centrifuged at 2500 rpm for 5 min. For collecting supernatant with MPs, the tube was placed in the crystallizing dish and the preferred solution (NaCl, as described in Section 3.3) was slowly added to overflow the supernatant with the least interrupting of the bottom layer. The collected supernatant was filtered through a glass fibre filter (pore size of 0.6 μm) in a vacuum filter system. To remove salt residues on the surface of MPs, we washed the filter paper with distilled water. The filter paper was then dried in an oven at 60 °C for 24 h.

2.5. Identification and quantification

For the recovery rate test, identification was not necessary as we spiked known MPs into soil samples. Reference MPs were analysed by TOC-SSM (Shimadzu, 5000 A, catalytic combustion at 680 °C and solid module combustion at 900 °C) to calculate carbon content in soil samples. As TOC-SSM measures absolute carbon content in the material, the glass fibre filter (theoretically no carbon content) was analysed to set the lowest carbon content. Calibration was conducted to calculate the carbon ratio with 1, 2, and 3 mg of reference MPs. The MP mass was determined based on Eq. (1).

$$m_{\mathrm{MP}} = \frac{m_C}{C_{MP}} \times 100 \tag{1}$$

Where: m_{MP} is the mass of the MPs.

m_C is the mass of carbon detected.

C_{MP} is the carbon content of the MPs (in percentage).

However, actual field samples require identification to determine the type, size, shape and colour of MPs. As identification of small-sized MPs

Table 1
Description of 10 soil samples.

ID	Location	Soil type	Topographical position and agricultural field use	pH		Organic carbon	ESP	EC
	Nearest town	**ASC**		**$CaCl_2$**	**water**	**%**	**%**	**dS m^{-1}**
S1	Clifton QLD	Vertosols	Mid slope grazing	5.9	7.0	1.28	0.9	0.039
S2		Vertosols	Flood plain cropping	6.9	7.9	0.96	1.9	0.152
S3	Pallamallawa NSW	Chromosols	Hill slope Cropping (fallow)	4.6	5.2	0.87	2.4	0.096
S4		Vertosols	Flood plain cropping (fallow)	6.1	7.2	0.76	1.6	0.083
S5		Vertosols	Flood plain cropping (fallow)	5.5	6.8	0.69	1.6	0.047
S6		Vertosols	Flood plain cropping (fallow)	4.9	5.9	1.02	2.4	0.068
S7	Goomburra QLD	Vertosols Dermosols	Flood plain grazing	6.3	7.2	2.02	2.4	0.070
S8		Ferrosols Dermosols	Knoll grazing	6.0	6.7	2.87	0.4	0.047
S9		Dermosols	Upper slope grazing	7.8	8.6	1.60	0.5	0.174
S10		Dermosols	Lower slope grazing	6.8	7.6	1.35	0.9	0.080

Note. ASC: Australian Soil Classification, ESP: exchangeable sodium percentage, EC: electrical conductivity.

is challenging, we first surveyed the field when collecting soil samples. The survey provided plastic residues on the surface of soils and the main plastic products in the field. Collected plastic residues were cleaned and identified by ATR-FTIR (type of polymer) and TOC-SSM (carbon content). Three different pore sizes of sieves (5, 2 and 0.3 mm) were used to separate field samples. In this way, we avoided optical counting for size distribution analysis. Considering the adhesive behaviour of MPs, we only used a 0.3 mm pore-sized sieve for a small size fraction. The extraction processes were the same as the recovery rate test (Fig. 1). The extracted MPs from farm soil samples were observed by microscopy with 100 × magnification (Olympus digital microscope, DSX-1000) to compare their shapes and colours of the collected plastic residues. Filtered and dried glass fibre filters were placed in a ceramic boat and analysed by TOC-SSM. Finally, MP mass was calculated based on the previously obtained carbon ratio and conversion equation.

2.6. Recovery rate

The spiked sample was a total of 30 g with 0.1 % (w/w) reference PE. The sample was weighed and divided into 12 subsamples for extraction and quantification. The procedure included three control groups without spiking reference PE. The recovery rate was calculated by Eq. (2).

$$Recovery\ rate(\%) = \frac{m_{Recovered}}{m_{Spiked}} \times 100 \quad (2)$$

Where: $m_{Recovered}$ is the recovered mass of the MPs.

m_{Spiked} is the spiked mass of MPs.

Potential losses may occur due to MPs adhering to the walls of labware, filtration through the membrane, and during the transfer of dried samples to the TOC-SSM sample boat. To address these issues, labware was optically inspected. A filter with a 0.6 μm pore size was also used to minimize the loss of MPs. Additionally, spiked samples were prepared using a larger quantity of soils (30 g in total, divided into 12 individual samples of 2.5 g each) to reduce the loss of lightweight MPs.

2.7. Quality control

All glass instruments and storage containers were washed and rinsed several times with distilled water and covered with a glass lid or aluminium foil. A cotton lab coat was worn through all processes in the laboratory to prevent any contamination from synthetic fibres. All reagents were checked for any impurities through filtration processes, including blank reagents. All analytical steps were conducted in a biosafety cabinet or fume hood to control airborne contamination of MPs. In the digestion of organic matter, three replicates were tested in each soil sample. For the TOC-SSM calculation (carbon content calculation and calibration), at least five to ten replicates were conducted.

2.8. Statistical analysis

IBM® SPSS® Statistics Version 28.0.1.0 (142) and OriginPro® 2024b (64-bit) Version 10.1.5.132 were used to analyse and plot data. Levene's test was used to check whether several groups have the same variance in the population before a comparison of means. For a comparison of the mean, Tukey's test was performed to find the overall difference and specific mean difference. The $P \leq 0.05$ level was employed to indicate a significant difference among the data.

3. Results

3.1. Reference MPs by milling

The mechanical milling method was applied to several PE products such as irrigation hoses and some commercial plastic bags. However, films were difficult to mill with a coffee grinder as they adhered to the wall of the grinder, only PE hoses were used for the reference MPs. Prepared PE-MPs were observed under a microscope and analysed by ImageJ software to match them to the target size ranges (less than 300 μm and 300–600 μm). The sieved reference PE sample (with a pore size between 300 and 600 μm) predominantly exhibited particle sizes between 300 and 600 μm based on particle numbers, while displaying the greatest degree of size variation from 100 to 1100 μm. This can be explained by the elasticity, electrostatics, and adhesion characteristics of polymers (Fig. 2). The ATR-FTIR analysis of reference PE (before and after milling) showed no significant change in the spectral bands by milling (Fig. 2c).

3.2. Digestion of organic matter

We chose the Piranha solution as the desired digestion method due to its relatively quick and strong reaction under low temperatures (See Supplementary Table S1 and Table 2). Other oxidative digestion required over 10 mL of total solution for a 2.5 g soil sample and demanded an additional filtering step before density separation. Without this filtering, dilution effects would occur in the subsequent density separation, complicating the process. Further, we observed yellow-orange colour residues on the surface of MPs after Fenton's reagent. Degradation by Piranha digestion was investigated via FTIR to identify any alteration in the chemical structure of PE.

The morphological changes of MP particles were observed by comparing photographs by microscopy before and after Piranha digestion and density separation protocols. Reference PE-MPs did not show destructive changes in their morphologies (Fig. 3a). Partial fragmentation may occur during digestion, but it is not clear whether fragments resulted from digestion or from existing particles that were adhered to the surface of other MPs. The ATR-FTIR analysis showed no significant alteration after Piranha digestion of PE-MPs (Fig. 3b).

Another important objective of digestion in our extraction method is to remove the total non-plastic carbon content in soils for TOC-SSM analysis. TOC-SSM calibration was undertaken with glucose (40 % of carbon by weight: 2 mg = 800 μg of carbon) and a glass fibre filter (theoretically containing no carbon). The calibration was also used for the carbon content analysis of MPs in the following sections (Fig. 4). The digestion results of soil samples (10 composite soil samples: ID from S1 to S10) showed high efficiency of Piranha digestion, and 5 samples resulted in 0 detections of carbon (Table 2). The negative value was considered a zero value, and other samples showed a negligible amount of detected carbon. The detected carbon content after digestion did not correlate with any of the soil properties such as organic carbon, exchangeable sodium percentage (ESP), EC and pH.

The detected carbon may represent MPs in soils as no soil sample is free from MPs [25]. Among the samples, the highest value was 8.71×10^{-4}% (equal to 8.71 μg kg^{-1}), which is considered a relatively ignorable value in the mg kg^{-1} quantification scale. This indicated that Piranha digestion effectively removed organic matter and potential sources of carbon for inflating MP concentrations in the analysis.

3.3. Density separation

High-density solutions like $ZnCl_2$ and NaBr reacted with H_2SO_4 and resulted in sedimentation that blocked the pores of the glass fibre filter, rendering $ZnCl_2$ and NaBr solutions unsuitable for density separation following pre-digestion with H_2SO_4 and H_2O_2. Additionally, these solutions are more costly and environmentally hazardous compared to NaCl. Therefore, NaCl (density of 1.2 g cm^{-3}) was selected as an optimal solution for density separation in this study, targeting PE (density < 1 g cm^{-3}) extraction. The density of NaCl is also suitable for separating other low-density plastics, such as polypropylene (PP, density 0.85–0.92 g cm^{-3}) and polystyrene (PS, density 1.04–1.06 g cm^{-3}), as these materials can still float in NaCl solutions [1].

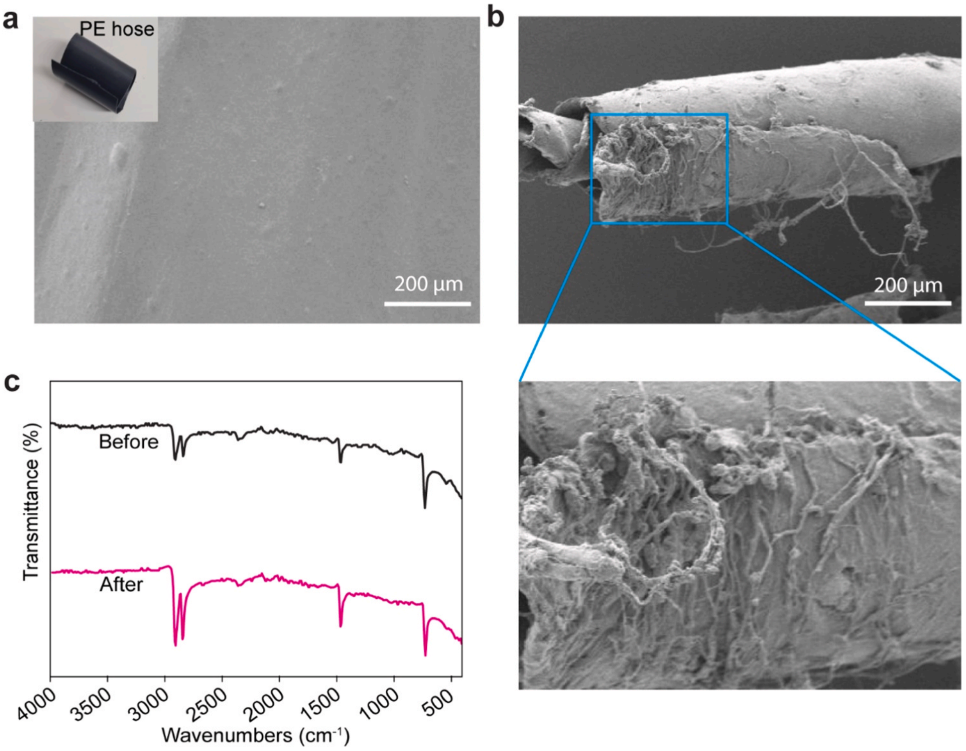

Fig. 2. a: The surface of reference polyethylene before milling; b: SEM image of milled reference polyethylene; c: FTIR comparison of reference polyethylene before and after milling.

Table 2
Piranha digestion efficiency tests by TOC-SSM.

ID	Detected area	Carbon mass (µg)	Carbon % (carbon/soil, w/w)
S1	16.2	32.9	6.58×10^{-4}
S2	17.6	43.5	8.71×10^{-4}
S3	9.50	−18.2	0
S4	9.41	−18.9	0
S5	10.5	−10.3	0
S6	10.3	−12.1	0
S7	17.6	43.5	8.71×10^{-4}
S8	16.1	32.2	6.43×10^{-4}
S9	11.2	−5.10	0
S10	11.9	0.409	8.15×10^{-6}

Note. Negative values were considered as below detection.

However, heavier plastics, such as polyethylene terephthalate (PET, density 1.34–1.39 g cm^{-3}) or polyvinyl chloride (PVC, density 1.3–1.58 g cm^{-3}), require higher-density solutions like $ZnCl_2$, NaBr, or $CaCl_2$ [1]. In these cases, it is critical to account for potential interactions between the digestion solution and the density separation solution. For example, Zn^{2+} and Ca^{2+} ions from these solutions may react with CO_3^{2-} or SO_4^{2-} ions, originating from the digestion step, water used during the process or the soil itself, and forming insoluble precipitates.

3.4. Recovery rate

After digestion and density separation, filtered and dried glass fibre filters were analysed by TOC-SSM. Carbon masses were detected, and the values were converted to MP masses. The irrigation hose (PE) contained 89 ± 0.9 (SE) % of carbon by pre-analysis with TOC-SSM (Table S4). Statistical tests (Levene's test for homogeneity of variances and Tukey's post-hoc test) confirmed that there is no significant difference in carbon content among different weights of PE (Tables S5, S6, S7). The recovery rates in 12 soil subsamples (each 2.5 g) were 97.39 ± 14.25 (SE) % for particle size between 300 and 600 µm and 94.80 ± 13.48 (SE) % for particle size less than 300 µm (Fig. 5b). The controls (soil without MP spike) resulted in between 0 and 40 µg, an ignorable amount relative to the spiked MP amount. The results suggested that the recovery rate increased with increased particle sizes [15,24]. The lower recovery rate of smaller particles may be caused by a possible loss during extraction: e.g., flying over while mixing and spiking MPs in soils or stuck on the devices (vacuum filtering) and glassware. However, a minor difference between the two ranges of size indicated that the TOC-SSM effectively quantified MPs regardless of the MP sizes.

Mixing the samples for 1 minute resulted in a diverse range of MP distributions across the subsamples, ranging from 974 to 5125 µg (Fig. 5a). The uneven distribution of MPs in spiked soil samples may suggest the possibility of high dispersion of MPs in actual soil samples, particularly those subjected to ploughing practices. This variability suggests that small subsample quantities might not adequately capture the full spectrum of MP contamination variability in soils. Various environmental factors such as rainfall, wind and human activities can also influence the distribution and concentration of MPs in soils. This finding highlights the importance of considering the potential variability in MP contaminations in conducting research or monitoring soils.

4. Application to field soils

4.1. Soil collection and survey

Real agricultural soil samples were collected from a strawberry farm using plastic mulch film in Stanthorpe, Queensland (Fig. 6). A transect sampling was conducted across the field using a 15 cm foot probe at multiple points to collect a composite sample. The collected composite sample was well-mixed and air-dried in the laboratory. The soil sample was transferred to a glass jar covered with aluminium foil and stored in the fridge before analysis. The soil from 0 to 10 cm depth has a texture of 92 % sand, 7 % of silt and 0 % of clay; and its pH measured in 1:5 soil water solution ($pH_{1:5}$) is 6.9 (at 25.2 °C); its $EC_{1:5}$ is 0.24 dS m^{-1}. The

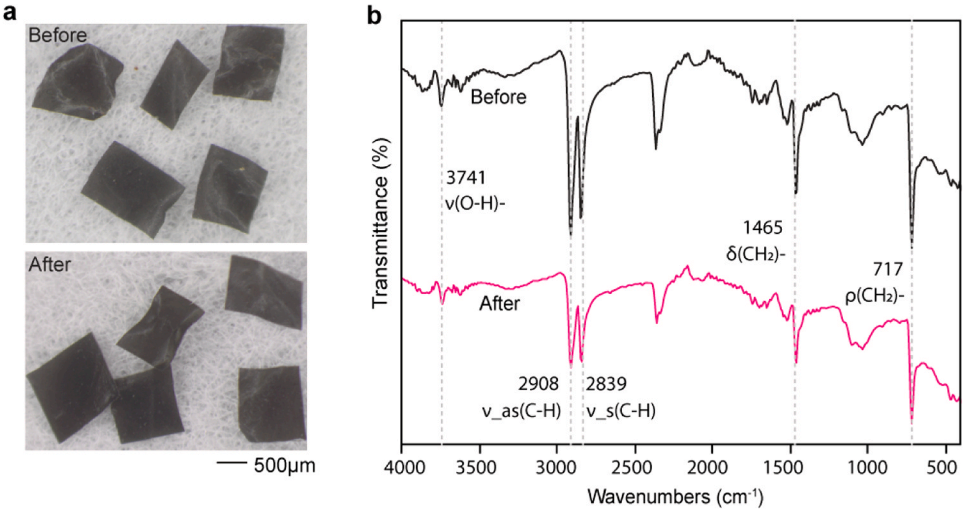

Fig. 3. Morphology (a) and FTIR (b) comparison of irrigation hose (polyethylene, used) before and after Piranha digestion (ν: stretching vibration; ν_as and ν_s: asymmetric and symmetric stretching vibration; δ: scissoring (bending) vibration; ρ: rocking vibration). The intensity was tested by normalized absorbance values and observed differences in indicative peaks (including carbonyl groups) were less than 2 % (See Supplementary Table S2). This suggests that the MPs remained chemically stable throughout the digestion process.

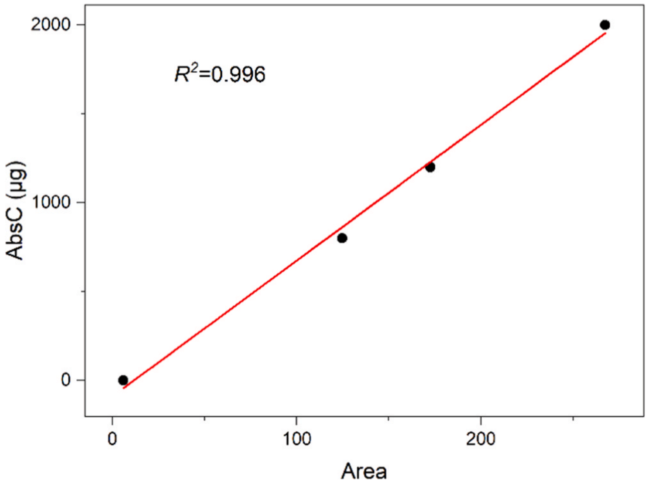

Fig. 4. Calibration of total organic carbon analyser-solid sample combustion unit (TOC-SSM). Calibration was conducted with glucose (2, 3 and 5 mg) and glass fibre filter (theoretically 0 carbon content); AbsC: absolute carbon mass in µg.

plastic residues via ATR-FTIR were identified to be PE. However, some residues could not be identified due to aging and degradation in the field (Fig. 7). The majority of residues were plastic mulch film with black colour and the carbon content was analysed by TOC-SSM to be: 87.1 ± 0.4 (SE) %.

4.2. Quantification of MPs

Microplastics with sizes between 2 and 5 mm were collected, cleaned, and weighed. A total of 850 µg MPs in the size range was found in the composited soil bulk sample (Table 3). For the extraction, 40 g of sample was chosen in case of low concentration of MPs in field soil samples. Each sample, initially weighing 40 g after sieving through a 2 mm sieve, was further sieved using a 0.3 mm pore size: each sample has two size ranges (between 0.3 and 2 mm and less than 0.3 mm size fraction). The extraction followed the procedures in Fig. 1 (field soil test) with 6 replicates. The carbon content was measured with collected residue plastic materials, black PE, 87.1 ± 0.4 (SE) % (See Supplementary Table S8). The concentrations of MPs (per soil weight) as determined by TOC-SSM were 12.24 ± 3.65 (SE) mg kg^{-1} for particles sized between 2000 and 300 µm; and 2.62 ± 0.66 (SE) mg kg^{-1} for particles sized less than 300 µm (Table 3). An example of optically identified particles by microscopy is presented in Fig. 8.

5. Discussion

5.1. Extraction methods

In the present study, extraction of PE-MPs by NaCl solution after Piranha digestion was confirmed to be effective. The Piranha digestion at 40 °C did not degrade PE-MPs and demonstrated powerful digestion efficiency on soils and the surface of MPs. A solution at a density of 1.2 g cm^{-3} was found to be adequate for separating low-density plastics such as PE. The quantification approach enabled us to calculate the weight of MPs in soils, achieving a recovery rate of over 90 %. Even relatively small-sized (< 300 µm) MPs achieved a similar recovery rate, indicating our proposed method's efficacy for extracting and quantifying PE-MP-dominated soil samples. The major sources of MPs in Australia are plastic mulch films (i.e., PE films) and biosolid applications [37]. Plastic mulch films are widely used in Australian horticultural fields and biosolids are typically applied in the cropping and grazing industry. Considering the potential MP contamination by the sources, the method can be applied to horticultural soil samples to quantify MPs [39].

Fenton's reagent left ferrous residues on the surface of plastics. In the case of aged plastics, the Fe residues have an increased tendency to adhere to plastics due to the altered surface properties over time and may interfere with the quantification processes [19]. A higher temperature (60 °C) helped accelerate the oxidative digestion reaction, but the reaction was extremely aggressive with some of the soil samples, causing MPs to float and adhere to walls of glassware. This issue necessitated an additional washing step as oxidative digestion required filtration before density separation. Small-sized MPs were trapped in the pores of the filtering membranes thus MPs were lost before density separation. In comparison, Piranha digestion (hydrogen peroxide and sulphuric acid) showed a relatively rapid reaction under lower temperatures in our extraction method (Table 2). Our preliminary tests showed that PE, PP, and PS were not affected by the Piranha digestion process, indicating its suitability for these low-density plastics. Additionally, Low-Density Polyethylene (LDPE) remained unaffected under Basic Piranha

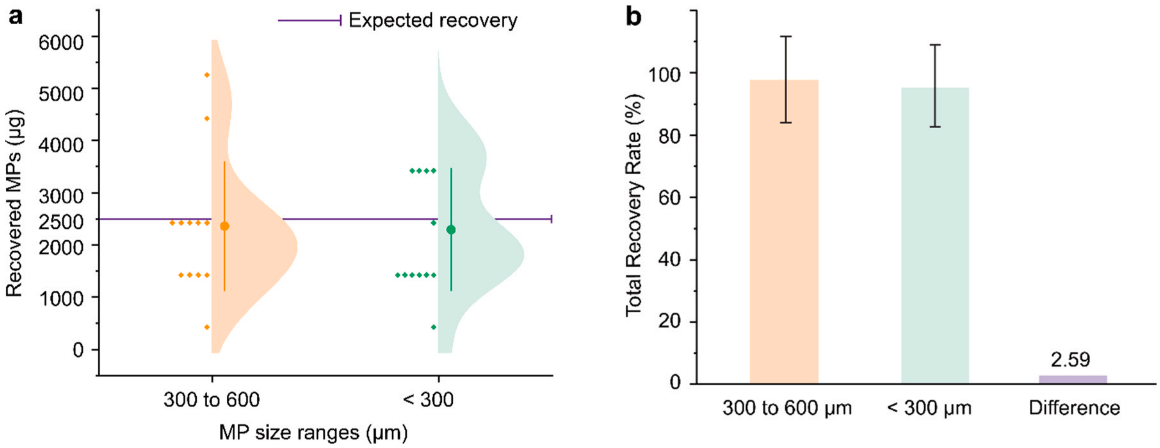

Fig. 5. Recovery of polyethylene (PE) microplastics (MPs). a) Distribution of the recovered MP mass (µg) for two MP size ranges: 300–600 µm (orange colour) and < 300 µm (green colour). Each dot represents an individual recovery (30 g of 0.1 % spiked soil sample, divided into 12 subsamples), while violin plot areas illustrate the density distribution of MP recovery. The central dot represents the mean recovery rate for each size group, while the vertical line indicates the mean ± 1 standard deviation (SD). The horizontal purple line represents the expected recovery. b) Total recovery rate (%) of PE-MPs for the two size ranges. Bars represent mean recovery rates with the error bar denoting SDs. The difference in recovery rates between the two MP size groups is quantified as 2.59 %.

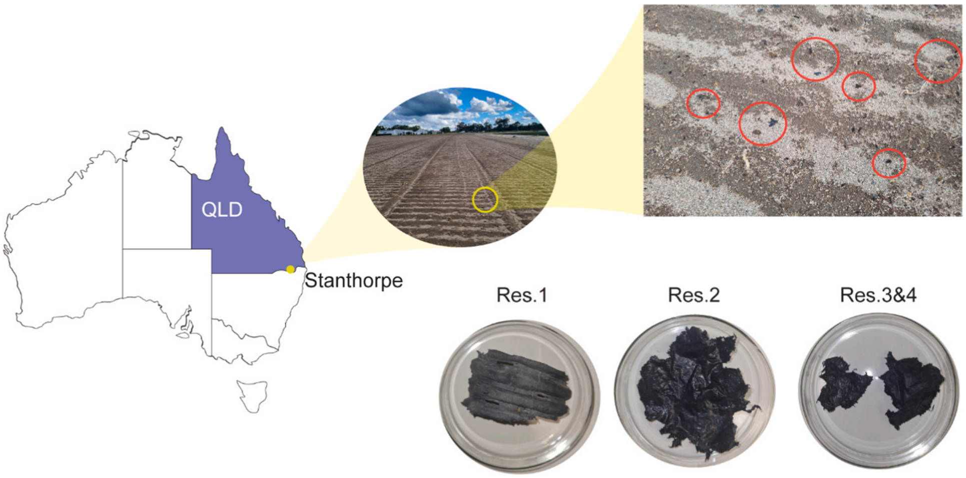

Fig. 6. Soil sampling location and collected plastic residues from the strawberry field (after removal of plastic mulch films). Residue 1 (Res.1): fragmented plastic; Res.2, 3 and 4: fragmented plastic mulch films.

digestion (H_2O_2 and NH_4OH), further supporting the stability of common low-density plastics under both acidic and basic Piranha digestion [30]. However, the method may not be suitable for all polymers. For example, PET showed size reduction and margin corrosion to hydrogen peroxide [36]. Thus, suitable digestion methods should be identified for specific polymer types before applying them to the extraction and quantification of MPs from collected plastic residues in targeted fields.

5.2. Identification of MPs

Identification of MPs larger than 100 µm was achieved by comparing the optical features of the plastic residues with those of extracted MPs from the agricultural field. However, numerous small particles, approximately 600 nm in size, were observed trapped within the pores of the membrane (Fig. 8). These particles were predominantly black, but their identity—whether plastic or other impurities—could not be determined visually. For accurate identification of small particles, the use of µ-FTIR or Raman spectroscopy is recommended [38]. It should be noted that some aged plastic materials from the fields produced ambiguous results in ATR-FTIR analysis, although they were still recognizable as plastic film by visual inspection. Given that spectroscopic analysis relies heavily on reference information, a thorough survey of the target field and collecting plastic residues are essential for accurate identification. This approach ensures that the reference materials used in the spectroscopic analysis are representative of the actual contaminants present in the environment.

While this approach helps to ensure the reference materials are representative of actual field contaminants, full representativeness remains uncertain due to the high variability of MPs in the field. Environmental degradation complicates the physical and chemical properties of MPs in soils, with each MP undergoing different stages of degradation. The variability in degradation stages can lead to differences in the functional groups on the surface and carbon content of MPs [2,3]. Although common MPs like PE, PS and PP are resistant to natural degradation in soils, their carbon content can still be altered over time, further complicating analyses such as FTIR, Py-GC-MS and TOC-SSM which rely on chemical signatures. Considering these challenges, residue collection should be consistent from comparable soil depth across the field and carefully designed sampling strategies should be adopted to reduce variability between field residues and MPs. This approach will improve the accountability of MP identification by providing clear reference features of dominant MPs in soils.

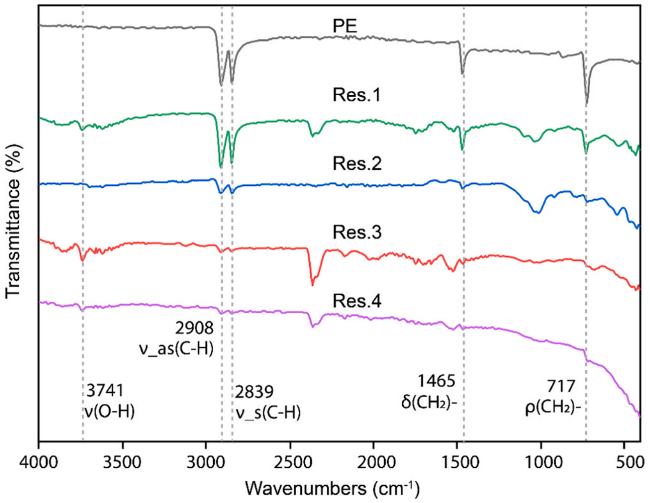

Fig. 7. FTIR results of field-collected plastic residues (Res.1 to 4). The FTIR spectra indicate degradation features by grey lines in polyethylene that align with findings from previous studies [3,6]. Developing O-H stretching vibration (ν) of hydroxyl (O-H) groups at 3741: this suggests chemical modifications or interactions with moisture or other environmental factors during the degradation process; Reduction of asymmetric and symmetric stretching vibration (ν_as and ν_s) of the methylene (-CH_2-) groups at 2908 and 2839: this suggests a reduction in the aliphatic chain length or the loss of aliphatic content due to degradation; Reduction of scissoring (bending) vibration (δ) of the methylene (-CH_2-) groups at 1465: this indicates that the methylene groups are being compromised or diminished as a result of the degradation process; Reduction of rocking vibration (ρ) of the methylene (-CH_2-) groups at 717: this indicates that the methylene groups are being affected, which could be due to cleavage of polymer chains or other chemical alterations.

Table 3

Microplastics quantified by the total organic carbon analyser-solid sample combustion unit (TOC-SSM) in Stanthorpe soil samples.

Size fraction (μm)	Detected Carbon mass (μg)	MP Weight (μg)	MP concentration in soils (mg kg^{-1})
5000–2000	-	850	150.44 ± 0.75[1]
2000–300	1026.489	1177.893 ± 4.71	12.24 ± 3.65[2]
	186.168	213.628 ± 0.85	
	318.931	365.973 ± 1.46	
	476.400	546.663 ± 2.19	
	344.704	395.546 ± 1.58	
	208.041	238.726 ± 0.95	
Less than 300	96.079	110.251 ± 0.44	2.62 ± 0.66[2]
	44.993	51.630 ± 0.21	
	50.500	57.948 ± 0.23	
	198.252	227.493 ± 0.91	
	73.519	84.363 ± 0.34	
	83.996	96.385 ± 0.39	

[1] Error due to scale precision (± 0.5 %).

[2] Standard deviation (SD) and standard error (SE) are applied based on the data context.

Note. Detected carbon mass was converted based on 87.1 ± 0.4 (SE) % carbon content in collected residue materials.

5.3. Quantification by TOC-SSM

The quantification results highlight the ability of TOC-SSM analysis for mass-based quantification of MPs. However, the TOC-SSM does not specify the lowest detection limit for carbon. For TOC-SSM analysis of soil, with a sample size limit of 1 g per sample boat and using the same detection system as TOC (4 μg L^{-1}, as specified in the manufacturer's guide), the detection limit would be approximately 4 μg g^{-1} of carbon in soil samples. Theoretically, a glass fibre contains no carbon, and the analysis showed consistent area values (ranging from 5.42 to 6.55), which established the lowest detection limit. The detected carbon value may originate from air or impurities in the pores of membranes.

Based on the recovered MP mass of subsamples, it appeared that soil samples spiked with < 300 μm MPs achieved a more homogenous mixing than the 300–600 μm MP spiked soil samples as no outlier samples were detected by the interquartile range method (Fig. 5a). This allowed us to test the sensitivity of the detection methods for MPs smaller than 300 μm. High variability of MP concentrations in the field conditions is likely due to differences in original MP depositions, dispersion factors such as rainfall, wind, human and animal activities and the high variability of soil properties at a fine scale. This variability, however, tends to decrease with the increase in sample numbers and sample size, demonstrating the importance of soil sampling strategies to achieve a representative sample.

The benefits of the TOC-SSM are its simplicity, cost-effectiveness, and ability to provide the actual weight of plastics, regardless of the size or the number of MPs. The maximum limit for carbon detection is 30 mg (as specified in the manufacturer's guide), which is equivalent to approximately 34.425 mg of reference PE-MPs (one teaspoon of our reference MPs weighed between 3 and 5 mg). This capacity is adequate for analysing the mass of MPs even in highly contaminated soil samples by adjusting the weight of the soil sample. Py-GC-MS is a reliable and accurate method to identify and quantify MPs with higher sensitivity than TOC, as indicated by its low limit of detection (e.g., 0.06 μg per injection) [18,26]. However, its relatively small sample size limits its effectiveness in providing a comprehensive understanding of MPs in soils. This limitation makes it less effective in addressing the uneven distribution of MPs in soils. In contrast, the scalability of the density separation and TOC-SSM method allow the quantification of larger soil samples, thus enhancing the representation of overall MP contamination in soils. While Py-GC-MS excels in quantifying smaller MPs, TOC-SSM provides a complementary approach for quantifying moderate to larger MP sizes, contributing to a more comprehensive understanding of MP contamination in agricultural soils.

However, the method can be limited by the efficiency in the digestion of organic matter. Black carbon, such as humic substances in soils, is a complex carbonaceous material formed from incomplete combustion [13]. Hydrogen peroxide can oxidize the black carbon, but the digestion efficiency may not be 100 %. The ultrasonification and centrifugation processes theoretically should fragment and sediment black carbon, given its density range of 1.8–2.1 g cm^{-3}. However, there is still a chance for black carbon to be attached to MPs or remain on a glass fibre filter, thereby being mistakenly included in the MP weight analysis.

5.4. Microplastics in agricultural soils

Our analysis of MP mass revealed the following concentrations for the strawberry farm surface soils: 150.44 ± 0.75 mg kg^{-1} for particles sized between 2000 and 5000 μm, 12.24 ± 3.65 (SE) mg kg^{-1} for particles sized between 300 and 2000 μm, and 2.62 ± 0.66 (SE) mg kg^{-1} for particles smaller than 300 μm. The results were similar to a previous report [12]. The total MP mass (around 165 mg kg^{-1}) in this work is also comparable to the MP concentration in an agricultural soil used plastic mulch film (white, PE) for over 30 years: approximately 101.3 mg kg^{-1} (5 year-mulched) and 291.78 mg kg^{-1} (15 year-mulched) [17]. Moreover, the descending trend of MP mass-concentration along with MP size

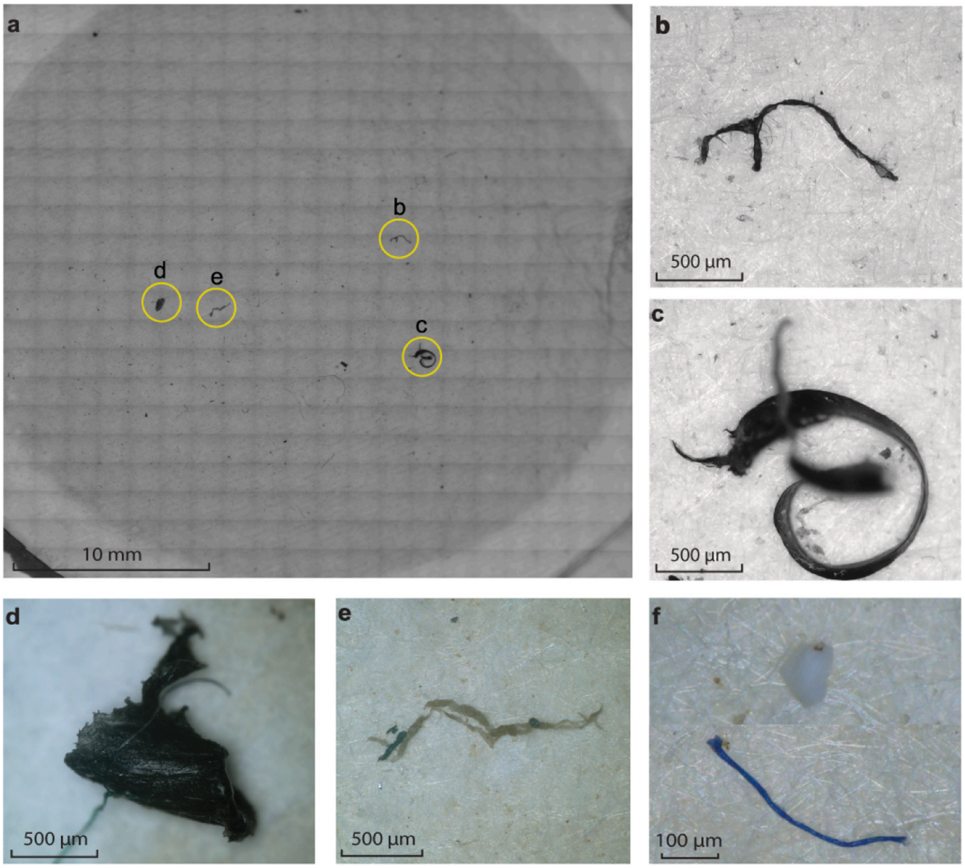

Fig. 8. Optical images of MPs (in the size fraction between 2000 and 300 µm) from field soil samples. Different filters and zoom scales were selected for clear observation of black and non-black particles. a) stitched image of extracted MPs on glass fibre filter, captured in high-quality panorama mode (10 % overlap, 20 by 20, 35.175 by 35.180 mm); b) Film fragment formed long (fibre-like) shape; c) Fragment; d) and e) Fragment with fibre-like shaped particle; f) Non-black particles.

is also consistent in their study.

In soil samples without a dominant type of MPs, where a mixture of various types of MPs is present, it may become more complicated to quantify MPs using this approach. Studies have shown that the accuracy of quantification decreases significantly with the increase in the diversity of MP types present in a sample [20]. The differences in their carbon content and resistance to digestion may lead to incomplete MP quantification. Therefore, additional research is required to verify and ensure the applicability and reliability of TOC-SSM to analyse various blends of MP-contaminated soil samples across different types of soil and agroecosystems.

While this study focused on TOC-SSM analysis validation and black PE film-dominated strawberry farm soil, future studies should explore the performance of TOC-SSM in analysing mixed MP types across different soil types, climates and agroecosystems to better understand its potential and limitations for broader applications. For example, recovery rate tests with known proportions and quantities of different MP types could provide insight into the accuracy of MP quantification. In the field residue analysis, optical sorting of collected residues could be employed to estimate the proportion of different MP types, providing a more practical approach for assessing MP quantification in soils. Additionally, the proportion of MP types in soils smaller than < 100 µm can be analysed using Py-GC-MS. Another aspect worth investigating is the relationship between recovery rate and MP size across different soil textures and organic matter contents. Although smaller MPs show a lower recovery rate, setting a boundary for minimum size in TOC-SSM analysis would be beneficial for accurate quantification. Additionally, employing a combined approach with TOC-SSM could help to increase the recovery rate for smaller MPs.

Accurate and practical assessment of MPs in soils enables regular monitoring of MP contaminations, enhancing our understanding of their long-term impacts, such as alterations in soil properties, microbial communities and crop productivity [10,21,37,43]. It also provides the necessary data to develop guidelines for effective management strategies to mitigate the potential adverse impacts of MPs in soils.

6. Conclusion

In this study, we have developed a robust method for extracting and quantifying dominant MPs in agricultural soils using TOC-SSM analysis. This method integrates an initial field survey, Piranha solution digestion for organic matter removal, density separation, and subsequent quantification. It was validated through high recovery rates of PE-MPs in the soil samples.

The optimized method was subsequently applied to measure MP contamination levels in soils from a strawberry farm where plastic mulch films are used. The quantified MP concentrations by TOC-SSM fall within the expected range of concentrations reported in previous studies on agricultural soils with plastic mulch films supporting the effective quantification of MPs in different sizes by this method.

Moreover, the proposed method allows the efficient quantification of MP mass in soils, providing crucial insights into the extent of MP contamination. Optical counting methods can be inaccurate, especially for small MPs. In contrast, TOC-SSM provides a more robust and scalable approach for mass-based quantification, accommodating a broader range of environmentally relevant MP sizes and larger sample volumes. Given the continuous usage of plastics and increasing concentration of MP contamination in agricultural soils, the method offers a credible quantification approach for monitoring MPs and complements existing techniques for risk assessment and environmental impact evaluation of

MPs in soils.

Environmental implication

Accurate quantification of microplastics (MPs) in soils represents a significant challenge due to the complex nature of organo-mineral matrix. Fine mineral particles and organic matter often interfere the efficiency of extraction, identification and quantification of MPs from soils. This study presents an improved approach for detecting and quantifying MPs in agricultural soils using the Total Organic Carbon analyzer - Solid Sample Combustion Unit (TOC-SSM). This method will help monitor MP pollution specifically in soils treated with mulch films, providing critical data for understanding the impact of plastic residues from mulch films on soil health and ecosystem dynamics.

CRediT authorship contribution statement

Chen Guangnan: Supervision. **Dearnaley John:** Writing – review & editing, Investigation, Formal analysis. **Wang Shaobin:** Writing – review & editing, Supervision, Methodology. **Liu Xiaohuan:** Writing – review & editing. **Song Pingan:** Writing – review & editing, Supervision, Conceptualization. **Seo Yoonjung:** Writing – original draft, Formal analysis, Data curation. **Lai Yunru:** Writing – review & editing, Methodology, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Australian Research Council (No. DP190102992, FT190100188).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2025.137841.

Data availability

No data was used for the research described in the article.

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