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Automated identification and quantification of invisible microplastics in agricultural soils

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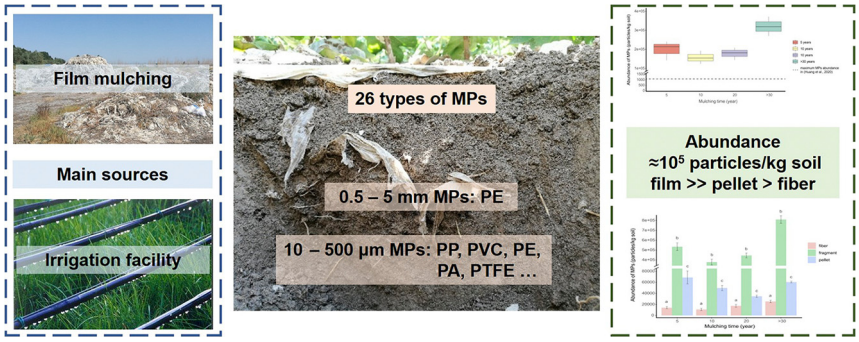
HIGHLIGHTS

- Using 8700 LDIR and ATR-FTIR to investigate the MPs in soil is rapid and accurate.
- The abundance of MPs reached 10^5 particles/kg soil in Xinjiang province.
- Totally 26 types of MPs are detected, and the majority were PP, PVC, PE and PA.
- Film mulching and irrigation are important sources of MPs in agricultural soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Microplastics in agricultural soils have become the research hotspot in recent years, however, the quantitative methods based on the traditional visual inspection may have a high false detection rate. Here we combined the laser direct infrared (LDIR) and Fourier–transform infrared (FTIR) methods to investigate the microplastics in farmland with long–term agricultural activities. The results showed that the total abundance of microplastics reached $1.98 \pm 0.41 \times 10^5$, $1.57 \pm 0.28 \times 10^5$, $1.78 \pm 0.27 \times 10^5$, and $3.20 \pm 0.41 \times 10^5$ particles/kg soil in cotton fields with film mulching of 5, 10, 20, and >30 years, respectively. LDIR results indicated that microplastics ranging from 10 to 500 μm accounted for 96.5–99.9 % of the total microplastic amounts in the soils. Additionally, a total of 26 polymer types of microplastics were detected, among which polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyamide (PA), and polytetrafluoroethylene (PTFE) were dominantly observed. For the microplastics detected by FTIR (500 μm–5 mm), PE polymer was majorly observed (88.0–98.9 %). Most microplastics were films (88.2 %), while fibers and pellets were also found. The reclaimed water from sewage treatment plants, the drip irrigation utilities, and the residual plastic film are the potential sources of microplastics in the farmland soils. By using the automated quantitative and identifiable approaches, this study suggested that the commonly used visual counting method may underestimate the microplastic contamination in agricultural soils.

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1. Introduction

Plastic products are advantageous because of their low cost, malleability, and durability. Global plastic production has increased from 1.7 million tons in 1950 to 368 million tons in 2019 (PlasticsEurope, 2020). However, only 9 % of the plastic was recycled, 12 % was burned, and the remaining 79 % was released into the environment (Geyer et al., 2017). Because of their refractory to biodegradation, plastics can remain in the environment for even centuries, where they are constantly broken and form small plastic particles under physical, chemical, or biological actions. Thompson et al. (2004) introduced the term microplastic in the study of plastic debris in the ocean. Microplastic is now universally acknowledged as plastic particles smaller than 5 mm (Wright et al., 2013). Since then, microplastic pollution has become an emerging environmental concern and the occurrence of microplastics in marine water (Jambeck et al., 2015), fresh-water (Frei et al., 2019), deep–sea sediments (Courtene-Jones et al., 2020), soil (Rillig, 2012), atmosphere (Dris et al., 2016) and even polar glaciers (Peeken et al., 2018) has been studied.

In comparison with the ocean ecosystem, it has been estimated that the amounts of microplastics released into terrestrial ecosystems are 4–23 times greater than those into the ocean (Horton et al., 2017). Farmlands may represent the core sinks of microplastics as they can enter agricultural soil through a wide range of routings, including plastic mulch, organic fertilizer application, artificial irrigation, and atmospheric deposition. Globally, approximately 20 million hectares of farmland are covered with plastic mulch (Steinmetz et al., 2016), and the main component of the plastic film is polyethylene (PE). After the functional period of mulching, the toughness of plastic film reduces, making it hard to recover. The remaining plastic film will be fragmented under multiple environmental conditions (e.g., ultraviolet radiation and physical disturbance), and ultimately form microplastics (Astner et al., 2019) in farmland soil (Fig. S1). Irrigation water, including surface water, groundwater, and purified sewage, is also an essential source of microplastics in agricultural lands. Massive abundance of microplastics accumulated in agricultural soils, potentially impacting the ecosystem functions. However, the microplastic concentrations used in the previous exposure studies were greatly manifold (approximately 0.01–28 % (*w*/w)), making it difficult to compare the study results to obtain the ecological baseline. The potential reason could be the methodological challenges in quantification.

A widely used method to quantify microplastics is visual inspection under stereoscope after flotation and further identification by Fourier Transform infrared spectroscopy (FTIR) (Huang et al., 2020; Liu et al., 2018; Zhou et al., 2020) or Raman spectroscopy (Chen et al., 2020; Feng et al., 2021). No matter which method is used for the microplastic identification, the quantification relies typically on the visual inspection under a stereoscope, which may have a 33 % false detection rate for 50–100 μm microplastics and a 37 % false detection rate for <50 μm microplastics (Lenz et al., 2015). Furthermore, the false detection rate increases with the microplastic size decreases (Nor et al., 2021). Therefore, a rapid and accurate method for the identification and quantification of microplastics in the soil is mandatory.

Among all the identification methods, Raman spectroscopy has a better size resolution (1 μm), but the background fluorescence of organic matter or pigments in polymers may strongly interfere with the required spectrum. Thus, this method may be an unfavorable choice of instrument for soil samples that contain rich organic matter. FTIR has a less precise size resolution (10–20 μm), but its spectral quality is not influenced by fluorescence, which may be more suitable for identifying microplastics from soils. The main FTIR technologies include FTIR in attenuated total reflection mode (ATR–FTIR), focal–plane–array FTIR (FPA–FTIR), and laser direct infrared (LDIR). ATR–FTIR requires the manual picking of suspected microplastic samples on the loading platform, which is more suitable for analyzing microplastics above 500 μm (Renner et al., 2017). Particles of 10–500 μm can be analyzed by FPA–FTIR (Löder et al., 2015) or LDIR. FPA–FTIR collects all the information on the test window, which is time–consuming. Comparatively, LDIR first scans the entire window and automatically identifies and locates all the particles on it, and then only collects the spectrum at the positions of the identified particles. Thus, only the valid data is collected and the detection speed is fast. Therefore, combining ATR-FTIR and LDIR may be a reliable method for microplastic identification and quantification in soil.

In this study, the cotton field with long–term film mulching in Shihezi City of Xinjiang Uygur Autonomous Region was selected. This field was all film mulched, highly mechanized, and centrally managed, making it possible to collect soil samples with different mulching times (i.e., 0, 50, 10, 20, and >30 years) while excluding other variables such as crop types. Techniques using laser Direct Infrared and total reflection Fourier–transform infrared methods were applied to detect microplastics ranging from 10–500 μm to 500 μm–5 mm, respectively. Furthermore, the distribution of abundance, particle size, polymer type, and shape of microplastics were investigated, and the possible source and migration ability of microplastics were critically discussed. This study will greatly enhance our understanding of the distribution and source of microplastics in farmland soil.

2. Materials and methods

2.1. Site description

The current study was conducted in Shihezi City, Xinjiang Uygur Autonomous Region, China (45°37′–44°17′N, 84°41′–86°18′E). Shihezi is located in the middle of Northern Xinjiang and has a temperate continental climate characterized by rare precipitation and extreme dryness. The annual average temperature is 7–8 °C and the annual precipitation is 180–270 mm. The farmland in this area is a typically irrigated agricultural area. The Eighth Agricultural Division of Xinjiang in Shihezi city introduced plastic film from Japan in 1980, carried out a demonstration in 1981, and started technical promotion in 1982. All cotton fields are covered with plastic film annually. According to China Rural Statistical Yearbook (Investigation Department, 2020), the amount of plastic film used in Xinjiang in 2019 had reached 242,684 t. The mulching rate of plastic film in the cotton fields can be up to 89.5 %, and the recovered rate could be approximately 80 %. The fertilization was dominated by chemical fertilizers. Drip irrigation, with a total amount of 4000–5000 m^3 per hectare per year, was applied to all cotton fields. The irrigation water had three local sources, Daquangou reservoir, Moguhu reservoir, and groundwater. Water in the Daquangou reservoir was the glacier meltwater from Tianshan Mountains, while the water in the Moguhu reservoir was from the effluent of sewage treatment plants. During the irrigation processes, the water consumption from the two reservoirs was greater than that from groundwater. All the buried pipelines and related materials in the drip irrigation systems are made of polyvinyl chloride (PVC).

2.2. Soil sampling

Samples were collected from the cotton fields with continuous film mulching in August 2019. Three cotton fields with 5, 10, 20, and >30 years of film mulching were selected in the planting areas of No.142 Construction Corps (44°26′N, 85°23′′E), No.133 Construction Corps (44°39′N, 85°16′E) and Shihezi Academy of Agricultural Sciences (44°20′N, 86°2′E) individually. Cotton fields with different years of film mulching were at least 100 m apart. There were 2 main sources of microplastics in the sampling area, film mulching, and irrigation. Films were fixed with soils and crops and were hard to contaminate fields 100 m away. Irrigation systems were trickling irrigation, therefore, wouldn't contaminate other fields. Moreover, there was little precipitation in the sampling area, therefore, contamination through surface runoff was unlikely to happen. At each field, three 5 m × 5 m quadrats were randomly placed. The soil cores (0–20 cm) were then collected from each quadrat and mixed thoroughly to make a composite sample per field. In total, 12 soil samples were collected. All samples were sealed in sterilized sampling bags for further laboratory analysis.

2.3. Sample processing

All these samples were air–dried and sieved through a 5 mm mesh (Fig. 1). The soil samples were then treated by digestion and the density separation method for microplastics isolation modified from the previous study (Huang et al., 2020). Relative information on MPs' recovery rate was provided in SI.

2.3.1. 10–500 μm MPs

For the extraction of 10–500 μm microplastics, five grams of air–dried soil were put in a glass beaker and dispersed thoroughly with 150 mL Fenton reagent for 3 h for the primary digestion. See Figs. S2 and S3 in the supplementary material for further information on digestion parameters. The beaker was then placed in an oven (101-1BS, Lichen, Shanghai) at 50 °C for 18–24 h until dry. Two hundred mL of saturated sodium chloride solution ($\rho = 1.2\ g/cm^3$) was added to the beaker, and the solution was agitated with a magnetic stirrer (120 r/min) for 30 min to completely disperse soil samples. After 24 h of static settlement at room temperature, approximately 100 mL supernatants containing microplastics were collected in a beaker and then filtrated through 500 and 10 μm stainless steel filter mesh by vacuum suction filtration system. Samples containing10–500 μm MPs needed secondary digestion and flotation to meet the machine standard of LDIR. The 10 μm filter mesh attached with 10–500 μm microplastics was placed in a 250 mL glass beaker and immersed with hydrogen peroxide (30 %, *v*/v). After ultrasonication (40KHz, 240 W) for 5 min, the filter mesh was rinsed with hydrogen peroxide (30 %, v/v) to remove all the attached residues. After 24 h of the secondary digestion, the beaker was placed in an oven at 50 °C for approximately 12 h until dry. Saturated sodium chloride solution was added into the beaker containing residues and then transferred the samples to a 500 mL glass separating funnel. The beaker was rinsed with saturated sodium chloride solution 3 times. After 24 h of static settlement at room temperature, the lower liquid containing soil particles was completely purged. The upper transparent solution was filtered with a 10 μm stainless steel filter mesh. The filter mesh was placed in a beaker, and the chromatographic grade ethanol(>99.5 %) was added to immerse it. After ultrasonication (40KHz, 240 W) for 5 min, the filter mesh was rinsed with ethanol and taken out. The ethanol solution containing microplastics was concentrated at 100 μL under nitrogen. The sample was stored in a 2 mL chromatography vial at 4 °C. For the quality control, all the experimental steps were carried out with the blank sample, the final sample solution was also stored in the 2 mL vial for further analysis.

2.3.2. 500 μm–5 mm MPs

For the extraction of 500 μm–5 mm microplastics, the primary digestion was the same. After the primary digestion, 200 mL saturated sodium iodide solution ($\rho = 1.78\ g/cm^3$) was added to the beaker, and then the whole solution was agitated with a magnetic stirrer (120 r/min) for 30 min to completely disperse soil samples. After 24 h of static settlement at room temperature, approximately 100 mL supernatants containing microplastics were filtrated through 500 μm stainless steel filter mesh by the vacuum suction filtration system. The filter mesh was then placed in an oven at 50 °C for approximately 3 h until dry.

2.4. Microplastic quantification and characterization

For the microplastics ranging 10–500 μm, the solution containing microplastics was ultrasonicated for 10–20 min. 20 μL of the sample was dropped on a glass slide (7.5 × 2.5 cm; MirrIR, Kevley Technologies) each time until all the liquid (100 μL) was transferred. After the ethanol was evaporated, the slide was analyzed by the automated LDIR (QCL) Imaging system (8700 LDIR, Agilent Technologies). The automated particle analysis protocol within the Agilent Clarity software (version 1.1.2) was used for all analysis. In the selected test area, the software used a fixed wave number at 1800 cm^{-1} to quickly scan the selected area and identified the particles (Fig. S4). The software automatically selected a non–particle area as the background, collected the background spectrum, and performed morphological identification and infrared full spectrum acquisition on the identified particles. Sensitivity was set to the maximum. After obtaining the particle spectrum, the software automatically made a qualitative

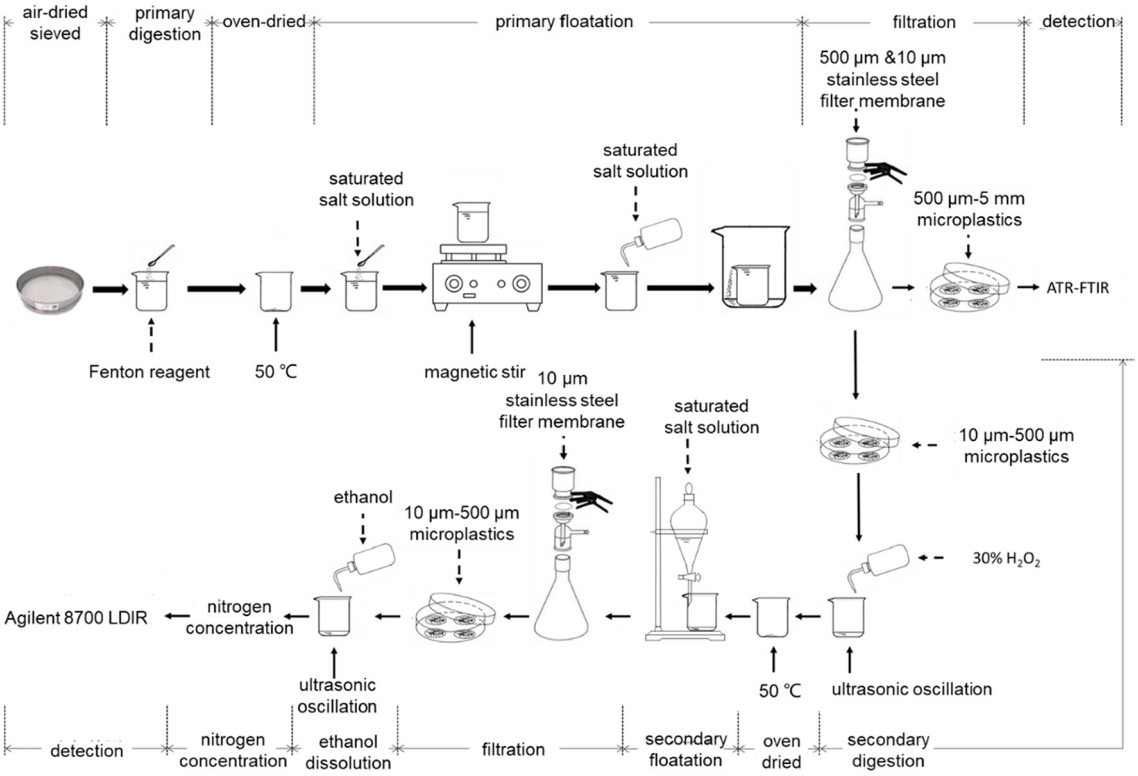

Fig. 1. Testing process of soil microplastics.

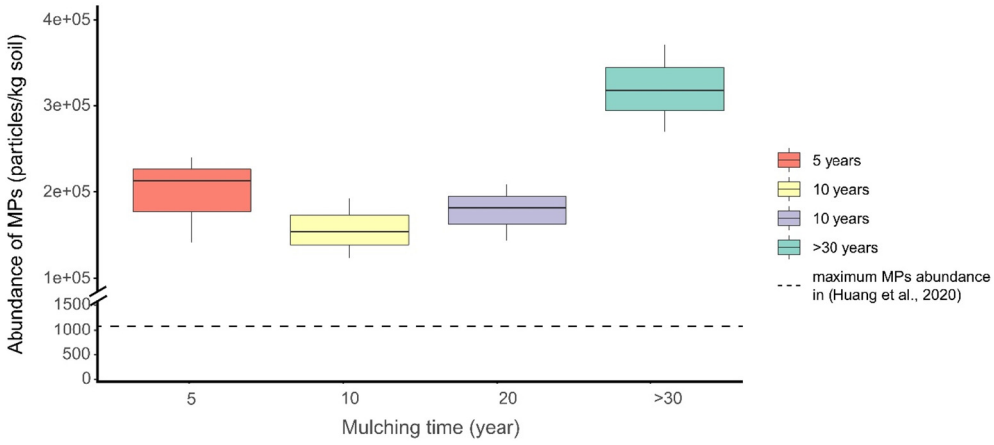

Fig. 2. The abundance of microplastics in agricultural soils at different film mulching times.

analysis with the standard spectra in the self-established database (Microplastics library 1.0) of Agilent. The setup was tested with standard PE pellets (100 μm, Duke Scientific, USA), and the hit quality index was >90 %. Considering the aging of MPs in environmental samples, hit quality was set to 65 % for identifying polymer compositions. Additionally, the information including the picture, size, and area of each particle was displayed in the quantitative results.

For the 500 μm–5 mm microplastics, the suspected microplastic particles were selected under a stereoscope (SZ61, Olympus, Japan). ATR–FTIR (Nicolet is50, ThermoFisher, USA) was used to further identify the polymer composition. The spectrum range was 400–4000 cm^{-1} with a spectral resolution of 4 cm^{-1}; 24 scans were performed. The spectra were compared to the standard spectra in the siMPle database (https://simple-plastics.eu). The polymer type, size, and shape (film, pellet, fiber) were recorded by the software.

2.5. Statistical analysis

Results from Agilent Clarity software included two shape–related indicators: circularity and solidity. In this study, pellets (≥0.6) and non–pellets (<0.6) were first distinguished according to circularity, and then fibers (<0.3) and films (≥0.3) were distinguished according to solidity. Since Agilent 8700 LDIR cannot detect microplastic thickness, fragment and film were not further distinguished. All statistical analysis was carried out in R language (version 4.1.1). The non-parametric Kruskal Wallis H test was used for a difference analysis, and the "kruskalmc" function in the "pgirmess" package was used for multiple comparisons with a significance level of 0.05. Principal component analysis (PCA) is made using the "stats" package.

2.6. Quality control

Stainless steel or glass containers and instruments were used for sampling and sample handling. All items were rinsed with Milli Q water and ethanol. Samples were processed on a clean bench. A control group was set up. For the control group, all the experimental steps were carried out without soil. MPs detected in the control group were 160 particles in total (Table S1).

3. Results

3.1. Abundance of microplastics in agricultural soils

In total, 47,453 particles were observed by LDIR and 34,124 of them were assigned as MPs. The recognition rate of MPs (10–500 μm) was 71.9 %. Any particle of which hit index was below 65 % was classified as "undefined". The undefined rate (undefined particles/all particles) represented the qualification of pretreatment. In this study, the undefined rates in all the samples were below 10 %, which meant the pretreatment was completely qualified. The spectra were given in Fig. S5. In the cotton field of Xinjiang, the average abundance of microplastics ranging from 10 μm to 5 mm was (2.13 ± 0.72) × 10^5 particles/kg soil (Fig. 2), which was 10^3 times higher than the previous visual results in similar cotton fields (Huang et al., 2020). The microplastics abundances were (1.98 ± 0.41) × 10^5, (1.57 ± 0.28) × 10^5, (1.78 ± 0.27) × 10^5 and (3.20 ± 0.41) × 10^5 particles/kg soil in the cotton fields with 5, 10, 20, and >30 years of plastic film mulching, respectively. Additionally, the average proportions of microplastics in different fields with sizes ranging from 10 to 50 μm, 50–100 μm, 100–500 μm, and 500 μm–5 mm were 50.83–97.49 %, 11.82–26.04 %, 1.38–7.85 %, 0.05–2.41 %, and 0.25–1.89 %, respectively (Table 1). A significant negative linear relationship between the logarithm of microplastic abundances and the logarithm of their sizes was observed (R^2 = 0.8184, $p < 0.001$) (Fig. 3).

3.2. Polymer types of microplastics in agricultural soils

In this study, 26 polymer types of microplastics were detected (Fig. 4). For the microplastic ranging 500 μm–5 mm, polyethylene (PE) accounted for nearly 100 % of the total counts of observed particles in all samples at this size range (Fig. 4). While for the microplastics with smaller sizes (10–500 μm), the polymer types were greatly diverse. Several types of MPs occupied a certain proportion. The top four microplastics in all samples

Table 1
Abundances and proportions of microplastics with different sizes at different film mulching times ×10^3 particles/kg soil (%).

Mulching time (year)	Size (μm)				
	10–50	50–100	100–200	200–500	500–5000
5	441.40 ± 100.32 (60.38–95.89)	101.60 ± 18.74 (14.67–21.30)	16.60 ± 7.21 (1.66–4.22)	3.87 ± 3.07 (0.14–1.23)	1.47 ± 1.37 (0.02–0.50)
10	322.33 ± 52.93 (60.12–83.74)	96.27 ± 21.06 (16.78–26.18)	20.33 ± 4.73 (3.48–5.59)	3.33 ± 1.00 (0.52–0.97)	5.87 ± 3.43 (0.54–2.08)
20	389.40 ± 40.63 (68.87–84.92)	85.53 ± 21.28 (12.69–21.09)	19.13 ± 6.94 (2.41–5.15)	4.60 ± 2.86 (0.34–1.47)	7.73 ± 5.99 (0.34–2.71)
>30	651.10 ± 74.68 (63.10–79.45)	177.13 ± 31.32 (15.96–22.82)	56.20 ± 19.05 (4.07–8.24)	18.20 ± 5.78 (1.36–2.63)	10.87 ± 1.95 (0.98–1.40)
Average	451.03 ± 141.89 (50.83–97.49)	115.13 ± 43.27 (11.82–26.04)	28.07 ± 19.67 (1.38–7.85)	7.50 ± 7.17 (0.05–2.41)	6.48 ± 4.99 (0.25–1.89)

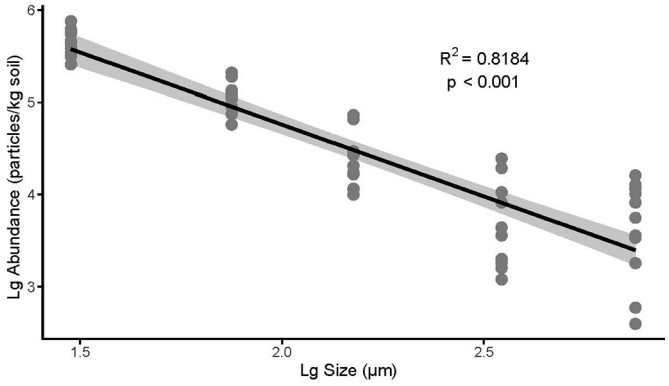

Fig. 3. Abundances of microplastics of different sizes in agricultural soils.

were polypropylene (PP, 23.84 ± 0.37 %), polyvinyl chloride (PVC, 23.4 ± 6.39 %), polyethylene (PE, 19.55 ± 2.03 %), and polyamide (PA, 17.16 ± 0.37 %). The relative abundance of polyoxymethylene (POM) was the fifth in the cotton field with 5 years of film mulching, while in other fields polytetrafluoroethylene (PTFE, 12.93 ± 6.09 %) was among the top five abundant microplastic types. Additionally, the proportions of PE, PC, and PTFE were relatively higher in the larger size ranges (e.g., 200–500 μm), whereas the proportions of PVC decreased following the increase in microplastic sizes.

3.3. Shapes of microplastics in agricultural soils

Due to the limitation of Agilent 8700 LDIR imaging, that is, the thickness of MPs could not be detected, and fragments were classified as films. As shown in Fig. 5, the abundance of microplastics with different shapes was film ≫pellet > fiber ($p < 0.05$), with film accounting for 88.2 %, pellet accounting for 9.0 %, and fiber accounting for 2.8 %. However, all the detected particles were films in the previous visual results in similar cotton

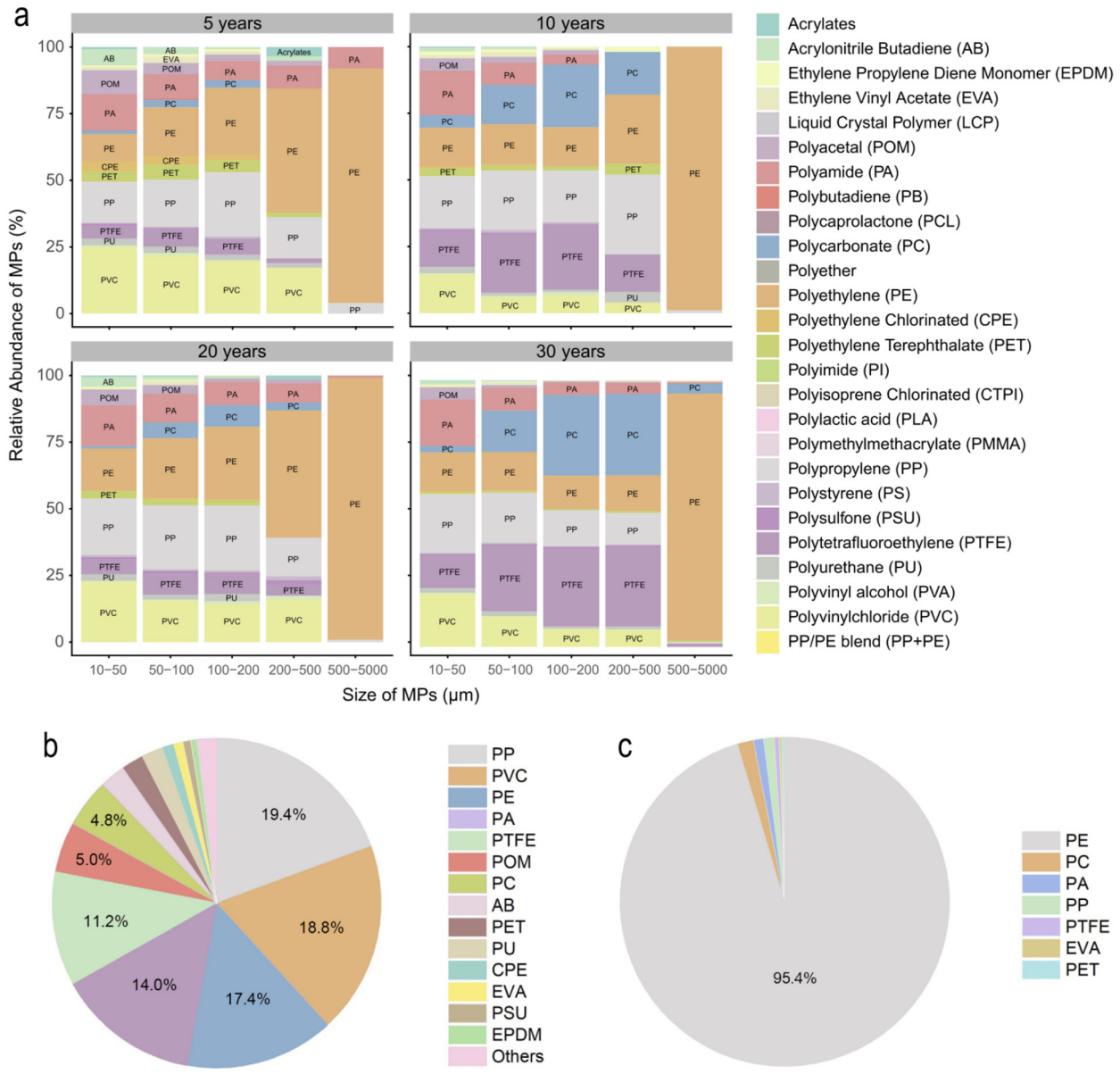

Fig. 4. Relative abundances of microplastics with different sizes at different film mulching times(a). Relative abundances of microplastics in 10–500 μm (b) and 500 μm–5 mm (c).

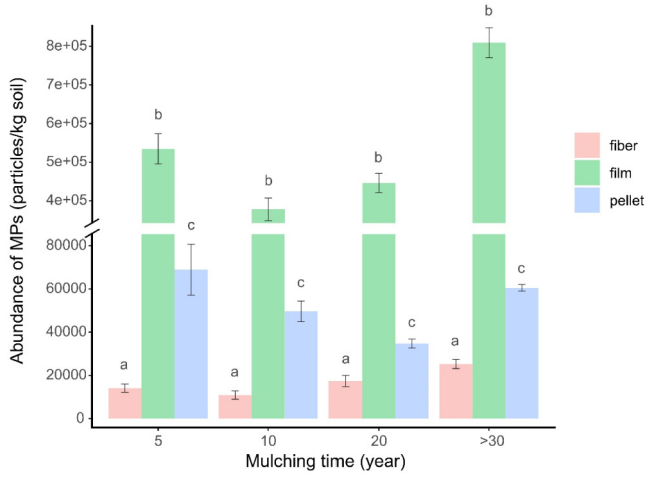

Fig. 5. Abundances of different shapes of microplastics in agricultural soils. Different letters indicate the differences at a significance level of 0.05, Kruskal–Wallis H test.

fields (Huang et al., 2020), which meant that the detection method could affect the findings of MPs shapes.

As shown in Fig. 6, PVC, PP, PE, and PA accounted for a relatively high proportion of the three shapes in all the soil samples. For instance, the proportions of PVC were 37.7 %, 25.3 %, and 13.8 %, respectively in fibrous, film, and pellet microplastics in the soil with 5-year mulching. PTFE also accounted for a relatively high proportion in the fibrous form in the soil with mulching years of 10 and >30 years. For all three shape categories of microplastics, the compositions of polymer types were greatly distinct. For example, in all the soil samples, the proportion of PA in the pellet was higher than that in the fiber and film, while the proportion of PP in the fiber was slightly higher than that in the film and pellet. In the soil with 20 years of mulching, the proportion of PVC in the pellet was more than those in the other shapes, while the proportion of PVC in other samples was fiber > film > pellet. The proportion of PTFE in the film was slightly higher than that in the fiber and the pellet. No clear pattern was observed for the rest of the polymer types.

4. Discussions

As is shown in Fig. 2, the exponential increase of microplastic abundances with the decrease of their sizes was observed, which is consistent with other studies (Nor et al., 2021). This may be caused by the further fragmentation of microplastics over time. Since microplastics in small sizes account for the vast majority, the detection limits of different quantification methods can significantly influence the findings of microplastics. To further understand the ranges of microplastic contaminations in agricultural soils, we performed literature research with respect to microplastic detection in farmlands (Table 2). The highest abundance in previous studies was 320–12,560 particles/kg soil (Chen et al., 2020), accounting for <1 % of this study. The abundance of microplastics in this study was 100–10^6 times higher than that in other regions. In addition to the different regions of sampling, the quantitative method also greatly impacts the results. For example, visual identification under stereoscope which is most commonly used in soil microplastics studies can cause high false-positive circumstances when it comes to small sizes (Table 2). It is generally believed that one can correctly identify microplastics only for particles above 100 μm (Nor et al., 2021), and the false detection rates grow with the size decrease. Although the FTIR, Raman spectroscopy, or heating method has been used to assist the microplastic identification, most studies did this process after visual detection, which may still ignore the particles with small sizes. We have previously conducted a microplastic quantitative study with the visually microscopical method in the same place (Huang et al., 2020). The result showed that the abundances of microplastics were 80.3 ± 49.3, 308 ± 138.1, 1075.6 ± 346.8 particles/kg soil, respectively, in the cotton fields with 5, 15, and 24 years of film mulching, and all particles were PE identified by FTIR. In the current study, different methods were used to quantify the microplastics in the soils located in the same

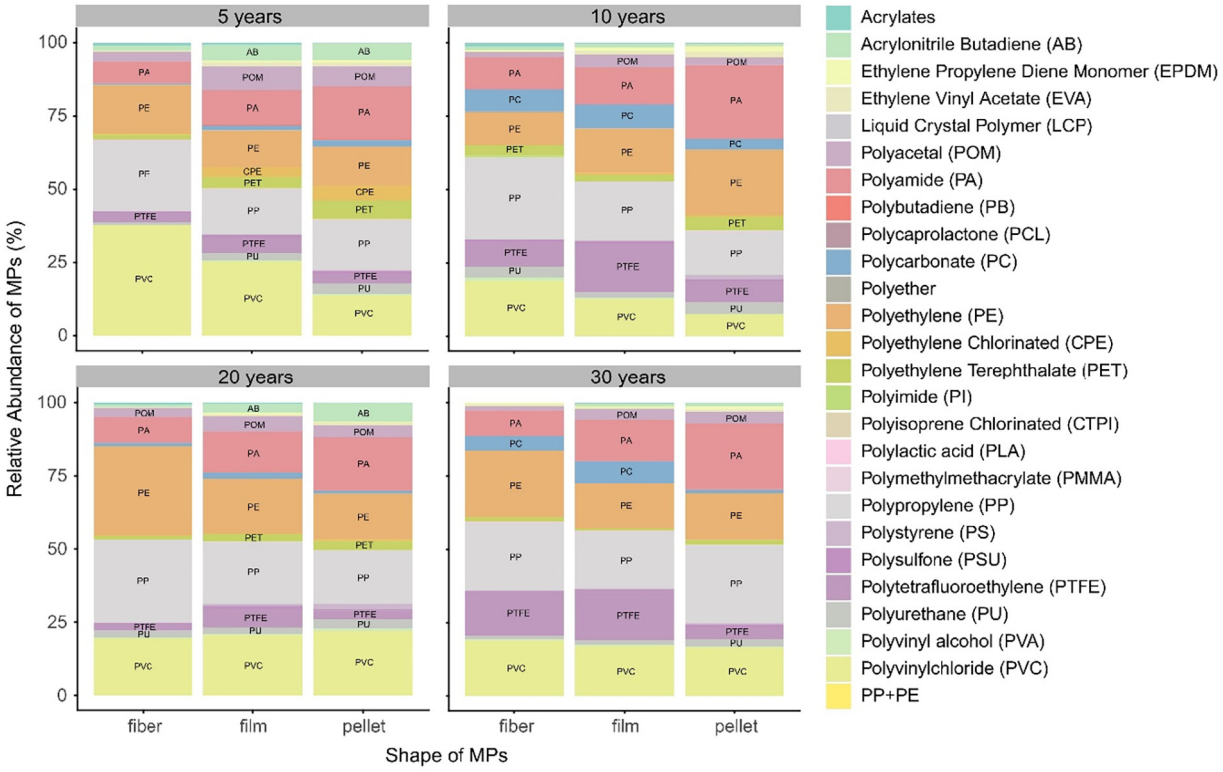

Fig. 6. Relative abundances of different shapes of microplastics at different film mulching times.

Table 2
Summary of research on the microplastic abundance in agricultural soils.

Location	Abundance (particles/kg soil)	Size range	Composition	Quantify method	Reference
Shihezi, Xinjiang, China	(1.98 ± 0.41) × 10^5, (1.57 ± 0.28) × 10^5, (1.78 ± 0.27) × 10^5, (3.20 ± 0.41) × 10^5	>10 μm	26 types (e.g. PP, PVC, PE, PA)	Agilent 8700 LDIR	This study
Shihezi, Xinjiang, China	80.3 ± 49.3, 308 ± 138.1, 1075.6 ± 346.8	>450 μm	PE	Stereoscope, FTIR confirmed	(Huang et al., 2020)
Loess Plateau, China	40 ± 126, 100 ± 141	>100 μm	PE, PP	Stereoscope, heating method (3–5 s at 130 °C)	(Zhang et al., 2018)
Middle Franconia, Germany	0.34 ± 0.36	>1 mm	PE, PP, PS	Stereoscope	(Piehl et al., 2018)
Shanghai, China	78.00 ± 12.91, 62.50 ± 12.97	>20 μm	PP, PE, PES	Stereoscope, μ–FTIR confirmed	(Liu et al., 2018)
Hangzhou, China	503.3 ± 509.2	>60 μm	PE, PP, Nylon, Polyester, Rayon, Acrylic, PA	Stereoscope, μ–FTIR confirmed	(Zhou et al., 2020)
Murcia, Spain	2116 ± 1024	<5 mm	/	Stereoscope, heating method (10 s at 130 °C)	(Beriot et al., 2021)
Southeast Mexico	870 ± 190	>10 μm	/	Stereoscope	(Huerta Lwanga et al., 2017)
Wuhan, Hubei, China	320–12,560	>20 μm	PA, PP, PS, PE, PVC	Stereoscope, micro–Raman spectroscopy confirmed	(Chen et al., 2020)
Qinghai–Tibet Plateau, China	53.2 ± 29.7, 43.9 ± 22.3	<5 mm	PP, PE, PS, PA	Stereoscope, Raman spectroscopy confirmed	(Feng et al., 2021)
Shouguang, Shandong, China	1444 ± 986	<5 mm	PP, PE	Stereoscope, μ–FTIR confirmed	(Yu et al., 2021)

region, planted with the same crop, and mulched with a similar period. A total of 26 polymer types of microplastics were detected, and the abundance was approximately 10^3 times higher than those reported in our previous study. Therefore, with a different detection method, our finding suggested that the previous quantitative studies of soil microplastics may seriously underestimate the abundances and types of soil microplastics.

Previous studies showed that the PE film mulching was a source of microplastics in farmland (Huang et al., 2020). The current study also observed that almost all microplastics with the size of 500 to 5,000 μm were PE film residual microplastics (Fig. 4c), which confirmed that mulching film was an important source of microplastics in agricultural soils. In the sampling region, where the sunshine is intense and the temperature difference between day and night is large, the plastic film was more susceptible to the harsh environmental conditions, become brittle, and fragmented into microplastics. The abundance of PE MPs ranging from 10 to 500 μm was about 100 times as much as that of PE MPs ranging from 500 μm −5 mm (Table S2). The abundance of PE microplastics in the soil with film mulching for >30 years was significantly higher than that in the fields with less film mulching time, suggesting that the residual microplastics from the film may continuously accumulate in the soil. However, there was no significant increase of PE films in the smaller size (10–500 μm) than in the larger size(500 μm–5 mm) in all samples. This may be due to the dynamic equilibrium of MPs fragmentation as well as the detection limit. New films are applied every year thus MPs with relatively large sizes continuously enter the fields, and meanwhile, MPs constantly break into smaller pieces. Due to the detection limit of LDIR, MPs smaller than 10 μm are undetectable. If MPs' detection technology breaks through the limitation of detection limit one day, the increase of PE films in smaller sizes may be observed. Considering that plastic film plays an irreplaceable role in agricultural production, future development of biodegradable film material would be essential. However, the polymer types of microplastics in 10–500 μm showed a significant difference from larger sizes (Fig. 4b), which suggested that microplastics with smaller sizes had other dominant sources. For example, irrigation was believed to be an important source of microplastics in farmlands (Yang et al., 2021), and may explain the high proportions of PP and PVC in this study. PP is one of the plastic types with the highest yield and consumption in the world (PlasticsEurope, 2020), which has been widely used in daily life, such as small appliances, toys, plastic bags, clothing, water supply, and heating systems. Therefore, previous studies have observed PP microplastics in the wastewater treatment plants. For instance, Wang et al. (2020) investigated the microplastics in the influents and effluents from approximately 25 wastewater treatment plants and reported that PP, PE, and PS made up almost 83 % of the total microplastics. In this study, the irrigation water was from the Moguhu reservoir, the confluence of the effluents of several sewage wastewater treatment plants. Even though we did not investigate the microplastics in this reservoir, considering the wide application and frequent detection, we may conclude that the PP microplastics detected in the cotton fields were from the irrigation water. Parallelly, all the buried pipelines in the drip irrigation system were PVC plastic. The small particles falling off from the drip system may contribute to the PVC microplastics in the soils.

This study indicated that the microplastics in soil were mainly distributed on the size of 10–50 μm, which could not be detected by visual counting methods. However, many studies have shown that fine-grained microplastics have a more serious negative impact on soil ecosystems (Rillig and Bonkowski, 2018). To establish the ecological baseline of microplastics, it is essential to establish a more precise standard detection method, and simultaneously study the environmental impact of microplastics with different particle sizes.

5. Conclusions

In this study, the abundance and composition of microplastics were investigated in the cotton fields with film mulching. The concentrations of microplastics increased with the mulching history and were 100–10^6 times greater than previous observations. A total of 26 polymer types of microplastics were detected, and the highest abundances were polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polyamide (PA). Three shapes, i.e., pellet, film, and fiber, were observed, while film microplastics were greatly dominant. Our results suggested both plastic mulching and irrigation system are important sources of microplastics in agricultural soils. Further studies with more accurate quantitative methods are necessary to deeper investigate the potential sources.

CRediT authorship contribution statement

Weiqian Jia: Data curation; Formal analysis, Investigation, Visualization, Writing - original draft, Writing - review & editing. **Aleksandra Karapetrova**: Writing - review & editing. **Mengjun Zhang**: Project administration, Visualization. **Libo Xu**: Writing - review & editing. **Kang Li**: Writing - review & editing. **Muke Huang**: Visualization. **Jie Wang**: Supervision, Writing - review & editing. **Yi Huang**: Funding acquisition, Project administration, Supervision, Writing - review & editing.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.156853.

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