Quantification and identification of microplastics in organic fertilizers: the implication for the manufacture and safe application

Jieru Xu
South China Agricultural University
Aiping Yang
South China Agricultural University
Yu Yan
South China Agricultural University
Yuqi Xu
South China Agricultural University
Minyi Tang
South China Agricultural University
Penghui Li
South China Agricultural University
Lanfeng Zhao
South China Agricultural University
Xinming Zhang
South China Agricultural University
Zongling Ren
zren@scau.edu.cn
South China Agricultural University https://orcid.org/0000-0003-1628-7897

Research Article

Keywords: Microplastics, Animal-derived organic fertilizer (AOF), Plant-derived organic fertilizer (POF), Treatment processes

Posted Date: March 11th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1332449/v1

Version of Record: A version of this preprint was published at Water, Air, & Soil Pollution on February 17th, 2024. See the published version at https://doi.org/10.1007/s11270-024-06977-x.

Abstract

The application of organic fertilizers has been suspected as an important source of microplastic (MP) pollution in agricultural soils. However, limited data have been reported regarding the quantity and characteristics of MPs in organic fertilizers, giving rise to the difficulties in their risk assessment. This study investigated the occurrence of MPs in 23 commercial organic fertilizers and 2 farm composts, covering different raw materials and treatment processes. The average MP concentration in the commercial organic fertilizers was 9210.4 ± 1743.1 items/kg, significantly lower than that in farm composts (24344.1 ± 2697.2 items/kg). Among commercial organic fertilizers, the MP loads varied significantly with the source materials and their processing. Organic fertilizers derived solely or proportionally from plant-derived materials through mechanical shredding and sieving had lower MP abundances. The polymer sizes, morphotypes, and colors of MPs in studied samples were mainly < 3 mm, fiber, and black, respectively. The variations in the MP characteristics implied their diverse sources. This study provided a detailed assessment of MP accumulation in organic fertilizers, and confirmed their significance to the MP pollution in terrestrial ecosystem. The results also highlighted the importance of establishing standards to regulate the contents of plastics in raw materials and end products and the treatment processes for the manufacture, thus ensuring the safe application of organic fertilizers.

1. Introduction

Agricultural soils are prone to accumulate microplastics (MPs) due to the multiple sources of plastics used in agricultural practices (Bläsing and Amelung, 2018; Hurley and Nizzetto, 2018). It was reported that the abundance of MPs in agricultural soils was up to 320-12560 items/kg in Wuhan, central China (Chen et al., 2020). The MP contamination in agricultural soils will alter plant's growth and developments, disrupt organisms' digestive/root system, disperse toxic compounds, etc. exerting adverse impacts on soil ecosystems and human health through food chains (Huerta Lwanga et al., 2017; Zhu et al., 2018; Okeke et al., 2022).

Organic fertilizers, which are made of plant-derived materials, animal manures, and agricultural by-products by aerobic composting and/or anaerobic fermentation, are rich in plant essential nutrients and organic carbon (FAO, 2019). The application of organic fertilizers is a widespread management practice in agriculture for enhancing soil sustainability and crop production (Bläsing and Amelung, 2018; Li et al., 2021). However, it has been estimated that organic fertilizer application may lead to an annual microplastic (MP) input of at least $3.5 \times 10^{10} - 2.2 \times 10^{12}$ items into the environment in Germany (Weithmann et al., 2018). Yang et al. (2021) found the long-term repeated application of pig manures significantly increased MP contents in an agricultural soil by nearly 3 times compared with unamended soil. Thus, organic fertilizers are a non-negligible contamination source of MPs into agricultural soils (Bläsing and Amelung, 2018; Weithmann et al., 2018). However, detailed studies regarding MPs in organic fertilizers are currently lacking.

The abundance and characteristic of MPs in organic fertilizers varies greatly among source materials and their processing. Due to the higher trophic level and more complex food sources of animals in food chains, manures are speculated to have more MPs with varied properties than crop wastes (Huerta Lwanga et al., 2017; Pérez-Guevara et al., 2021). 129.8 ± 82.3 × 10^3 items/kg MPs and 997 ± 971 items/kg MPs were found in chicken feces from traditional Mayan home gardens in Southeast Mexico (Huerta Lwanga et al., 2017) and sheep feces from the intensive vegetable farming in Southeast Spain (Beriot et al., 2021), respectively. By contrast, Weithmann et al. (2018) only found negligible amounts of MPs (0–11 items/kg dry weight) in the end-of-process digestates from 11 agricultural biogas plants mainly processing regular energy crops and about 20 items per kilogram dry weight in the 8 mm and 15 mm sieved composts from a composting plant processing household waste together with green clippings in Germany, not taking < 1 mm MPs into account. Therefore, it is important to obtain the detailed information of MPs, such as the abundance, size, and polymer type, in both raw materials and end-product fertilizers for the qualified production and the safe application in agriculture (Bläsing and Amelung, 2018; Yang et al., 2021).

Although organic fertilizer has been believed to be an important vehicle for the entry of MPs into agricultural soils, there is limited data available on the presence of MPs in organic fertilizers to support this conclusion, partly due to the difficulties in effective analysis of MPs in the complex and organic-rich substrates (Hurley et al., 2018; Nguyen et al., 2019). Organic matter usually adheres to MP particles, hindering the identification of MPs during visual sorting and spectroscopic analysis (von Sperber et al., 2016; He et al., 2018). Besides, the densities of organic matter are close to those of some plastic types and it may impact the effectiveness of density separation for MPs (Bläsing and Amelung, 2018). Therefore, it is critical to remove organic matter before the density separation for extracting MPs from organic fertilizers. Hurley et al. (2018) compared 30% (v/v) H_2O_2, 1M and 10 M NaOH, 10% KOH, and Fenton's reagent for the removal of organic material from soil and sludge samples, and validated Fenton's reagent as the optimum protocol without significantly affecting the MP extraction efficiencies. While extracting MPs from feces sample, Yan et al. (2020) found Fenton's reagent cannot fully digest feces solids, and then 65% HNO_3 was incorporated to digest the remaining solids. However, it is still unclear if these protocols can be efficient for the MP extraction from organic fertilizers.

Giving that the extensive use of inorganic fertilizers has greatly decreased soil quality and deteriorated the environment, the use of nutrients from reused or recycled organic materials is widely encouraged (FAO, 2019). Especially in China, the government has launched soil organic matter enhancement project (MOA, 2012) and Organic-Substitute-Chemical-Fertilizer (OSCF) action (MOA, 2017) to promote the use of organic fertilizers in order to enhance soil health and fertility (Yi et al., 2021). From 2004 to 2014, the sales of organic fertilizer had increased more than 20 times in China (Du et al., 2020). Under such circumstances, the investigation of MPs in the organic fertilizers is quite necessary. In this study, MPs were extracted from 23 commercial organic fertilizers and 2 farm composts, which were processed differently from a variety of organic wastes that ranged from plant materials to animal manures and litters to agricultural by-products. The abundance, polymer size, type, and morphology of MPs were then investigated by visual sorting and Raman spectroscopy. Our objectives are to (1) compare the MP accumulation in different types of organic fertilizers (animal-derived versus plant-derived, naturally composted versus mechanically processed), thus providing suggestions on the choice of raw materials and processing technology for the manufacture of organic fertilizers; (2) evaluate the potential impact of applying organic fertilizers on the spread and fate of MPs in soils.

2. Materials And Methods

2.1 Sample Collection

In this study, 23 commercially available organic fertilizer samples were purchased from different manufacturers or distributors in China, and 2 farm composts (FC) serving as the non-commercial fertilizer references were collected from different farms in Canton, China. All the samples were already air-dried. The information of raw materials and processing procedures for each fertilizer was obtained through inquiring of the manufacturers or distributors and observing the appearance of samples.

As shown in Table 1, the commercial organic fertilizers were categorized into three types, i.e., animal-derived organic fertilizer (AOF), plant-derived organic fertilizer (POF), and organic fertilizer made from the mixture of plant- and animal-derived materials (APOF) according to their source materials. Finally, 11 AOFs and 10 APOFs were collected, whereas only two POFs were found because very few organic fertilizers on the market were solely made from plant-derived materials due to their low nutrient contents. Moreover, the fine-textured and homogeneous fertilizers were normally mechanically treated, while the coarse-textured and clumped fertilizers in which the residues of original materials could be frequently found were naturally composted.

Table 1

Raw materials and processing procedures of different organic fertilizer samples analyzed in this study [a]

Sample	Types	Raw materials	Processing procedures
1	Commercial AOF	Chicken feces	Mechanical shredding and sieving (> 5mm)
2	Commercial AOF	Chicken feces	Mechanical shredding and sieving (< 5mm)
3	Commercial AOF	Chicken feces	Mechanical shredding and sieving (< 5mm)
4	Commercial AOF	Chicken feces	Natural composting
5	Commercial AOF	Sheep feces	Mechanical shredding and sieving (< 5mm)
6	Commercial AOF	Sheep feces	Natural composting
7	Commercial AOF	Sheep feces	Natural composting
8	Commercial AOF	Cattle feces	Mechanical shredding and sieving (> 5mm)
9	Commercial AOF	Cattle feces	Natural composting
10	Commercial AOF	Cattle feces	Natural composting
11	Commercial AOF	Pig feces	Natural composting
12	Commercial APOF	Fish wastes and peat, 1:9 w/w	Mechanical shredding and sieving (< 5mm)
13	Commercial APOF	Fish wastes and peat, 1:19 w/w	Mechanical shredding and sieving (< 5mm)
14	Commercial APOF	Chicken feces, soybean meal, bone meal, and plant ash	Mechanical shredding and sieving (> 5mm)
15	Commercial APOF	Chicken feces, rice bran, and distillers' grains	Mechanical shredding and sieving (< 5mm)
16	Commercial APOF	Chicken feces and mushroom residues	Natural composting
17	Commercial APOF	Pig feces and coconut peat	Mechanical shredding and sieving (< 5mm)

[a] AOF: animal-derived organic fertilizer; POF: plant-derived organic fertilizer; APOF: organic fertilizer made from the mixture of plant- and animal-derived materials.

Sample	Types	Raw materials	Processing procedures
18	Commercial APOF	Pig feces and mushroom residues	Mechanical shredding and sieving (< 5mm)
19	Commercial APOF	Pig feces, coconut peat, and rice husk	Natural composting
20	Commercial APOF	Bone meal, sugarcane bagasse, and peanut press cake	Mechanical shredding and sieving (< 5mm)
21	Commercial APOF	Rabbit feces and mushroom residues	Natural composting
22	Commercial POF	Tobacco leaves	Mechanical shredding and sieving (> 5mm)
23	Commercial POF	Soybean meal	Mechanical shredding and sieving (< 5mm)
24	Farm compost	Cotton straws and mushroom residues	Natural composting
25	Farm compost	Chinese medicine residues and mushroom residues	Natural composting

[a] AOF: animal-derived organic fertilizer; POF: plant-derived organic fertilizer; APOF: organic fertilizer made from the mixture of plant- and animal-derived materials.

2.2 Extraction of MPs

Three 1-kg subsamples were taken for each fertilizer or compost, and were gently crumbled to pass through a 5-mm sieve. Macroplastics (> 5 mm) were collected and rinsed thoroughly with Milli-Q water and 30% ethanol. MPs in the fertilizers or composts were then separated and extracted according to the method adapted from Hurley et al. (2018). In brief, 10 g of each subsample was placed into a prewashed 1 L glass beaker. With continuous stirring, 10 mL of Fenton's reagent, which was composed of 30% (v/v) H_2O_2 and 2%(w/v) $FeSO_4 \cdot 7H_2O$ (pH = 3) at the ratio of 1:1, was added into the beaker 10 times or more until no reaction occurred. An ice bath was used to keep the temperature below 40℃. Following the digestion, the overlying liquid was vacuum filtered onto a glass fiber paper. The residues in the beaker were mixed with 100 mL saturated NaCl solution (ρ = 1.2 g/cm^3), and the suspension was then stirred and ultrasonically treated for 15 min. After standing for 24 h, the supernatant was filtered through the glass fiber paper. The same floating and separating procedures using saturated NaCl were repeated three times for the same subsample. Then the extracted particles on the filter were rinsed with Milli-Q water and 30% ethanol. Finally, the filter was dried at room temperature and stored in a glass petri dish for MPs identification.

2.3 Identification and Characterization of MPs

The extracted particles on the filters were counted and measured using a stereomicroscope (LEICA M165 C) at 10× − 40× magnification. Suspected MPs were identified according to their color, shape, hardness, and luster. The abundance, shape, color, and size of MPs for each sample were recorded. According to their morphologies, MPs were classified as fiber, fragment, film, and pellet (Hidalgo-Ruz et al., 2012; Li et al., 2018). The size was divided into four range of < 1, 1–3, 3–5, and > 5 mm, since some entangled MPs such as fibers were actually longer than 5 mm.

For each sample, 4–5 representative MPs were selected using stainless steel tweezers to constitute a set of 114 MP samples, covering all the morphotypes. The polymer type of the 114 MPs was identified by Raman spectroscopy (LabRAM HR800, Horiba Jobin-Yvon, France). For the instrument settings, 632.817 nm excitation laser, grating with 600 grooves/mm, 10 s integration time, and 200 μm hole size was used, and spectral range was set to 100–4000 cm^{-1} (Imhof et al., 2016; Munno et al., 2020). System calibration was performed by zero-order correction of the grating and additionally on the 520.7 cm^{-1} peak of a silicon wafer (Imhof et al., 2016). The measured spectra were identified by comparison with reference spectra from a custom-made spectral polymer library, which included the most common plastic polymers, such as polyethene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS), polyamide (PA), polycarbonate (PC), acrylonitrile butadiene styrene (ABS), cellulose acetate (CA), and polyethylene-vinyl acetate (PEVA), etc.

2.4 Quality Control and Quality Assurance

Strict control measures were adopted during sampling and laboratory analysis. Separation and extraction of MPs were conducted in a laboratory with air filter and restricted access. The wearing of cotton clothes and nitrile gloves was required during the experiment. All the solutions were filtered prior to use. The labware was rinsed with Milli-Q water and pre-filtered ethanol, then wrapped with aluminum foil. All the samples and filters were always covered with aluminum foil to minimize possible contamination. Three procedural blanks were also performed alongside the samples, and no contamination of exogenous MPs was found in the blank samples.

The method for extracting MPs was first validated through a recovery test of four analytical grade MPs (PA, PET, PP, and PE) (Table S1), and the recovery rates were 100%, 100%, 97.33%, and 98.67%, respectively (Table S2). Moreover, Fenton's reagent did not cause significantly degradation of the tested MP particles (Figure S1). The results of our recovery test were consistent with previous results (Hurley et al., 2018), and confirmed this method was suitable for extracting MPs from organic fertilizer samples.

2.5 Statistical Analysis

Statistical analysis was conducted using SPSS Statistics 23.0. Since the collected data did not follow a normal distribution, the nonparametric Kruskal-Walllis H test was performed for multiple comparison of the MP contents in three varieties of commercial fertilizers as well as in the farm composts, and the Mann Whitney U test was performed for pairwise comparison of the MP contents between AOF and APOF. Differences at $p < 0.05$ were considered to be statistically significant.

3. Results And Discussion

3.1 Abundance of MPs in Different Organic Fertilizers

MPs were observed in all the commercial organic fertilizers ranged from 4266.7 ± 2274.5 to 18028.6 ± 2000.0 items/kg with mean content of 9210.4 ± 1743.1 items/kg (Fig. 1 and Table S3). The MP loads of the commercial fertilizers were significantly lower than those in farm composts (24344.1 ± 2697.2 items/kg) ($p < 0.01$). It indicated that the source inputs and processing environment of the mass-produced commercial organic fertilizer were more strictly controlled than those of farm composts, which were composted in the backyard and may be easily contaminated with MPs from private household wastes, road runoff as well as atmosphere deposition (Huerta Lwanga et al., 2017).

The abundances of MPs in the commercial organic fertilizers varied with the source materials (Fig. 1 and Table S3). The MP contents in AOFs (10692.6 ± 3353.3 items/kg) were significantly higher than those in APOF (7914.2 ± 4444.3 items/kg) and POFs (7539.5 ± 2779.9 items/kg) ($p < 0.01$), suggesting that the plant-derived materials were less contaminated with plastic items compared with animal manures (Weithmann et al., 2018). Therefore, their mixing not only promoted the composting process and the compost quality (Afonso et al., 2021), but also reduced the potential pollution risk of MPs from the application of organic fertilizer. As shown in the APOFs derived from peat and fish wastes (samples 12 and 13), the MP contents decreased with the increased mixing ratio of peat (Table S3).

Moreover, there was little difference in average MP concentrations among the AOFs derived from different types of animal manure (chicken, sheep, cattle, and pig), no matter they were naturally composted or mechanically processed (Table S3). Compared with the AOFs made from the same type of manure, the corresponding APOFs had significant lower MP concentrations except the naturally composted (samples 16, 19, and 21) (Table S3). One possible explanation was that under natural conditions the plant-derived materials, such as mushroom residues and coconut peat, may contain a certain number of plastics that could be removed during mechanical processing. Unfortunately, the MP content in naturally composted POF or plant-derived raw material was not determined in this study. But the high contents of MPs in the farm composts both made from plant-derived materials may provide some support for the explanation.

The MP abundances found in this study were close to those in dewatered sewage sludge from waste water treatment plants (WWTP) (Mahon et al., 2017; Zhang et al., 2020; Liu et al., 2021), rather than most reported MPs amounts in the comparable samples, such as pig manure from Southeast China (1250 ± 640 items/kg) (Yang et al., 2021), sheep feces from Southeast Spain (997 ± 971 items/kg) (Beriot et al., 2021), biowaste digestion from Germany (14–895 items/kg) (Weithmann et al., 2018), and sewage sludge composts from South China (254.6 ± 84.1 items/kg) (Zhang et al., 2020) (Table 2). This difference could be partly due to the variation of source materials and their treatment processes (Mahon et al., 2017; Li et al., 2018; Weithmann et al., 2018). The more efficient extraction by using Fenton's reagent could be another reason for the high abundances of MPs in this study, since there was lack of the pre-treatment of organic matter in the matrices in the previous studies (Weithmann et al., 2018; Zhang et al., 2020; Beriot et al., 2021; Yang et al., 2021). In addition, some aging MP particles might be degraded or sheared as well during the contact with Fenton's reagent, thus increasing the contents of small-sized MPs (Nuelle et al., 2014; Mahon et al., 2017; Bläsing and Amelung, 2018).

Table 2
Summary of abundances and characteristics of detected MPs in different organic fertilizers, composts, and their source materials

Location	**Type**	**MP abundance**	**Shape**	**Size range**	**Polymer type**	**References**
Traditional Mayan home gardens in Southeast Mexico	Chicken feces	29.8 ± 82.3 × 10^3 items/kg	-	0.1-1 mm	-	Huerta Lwanga et al., 2017
Composting plant, Germany	Structure compost	2.38 mg kg^{-1} dry weight	-	-	-	Bläsing and Amelung, 2018
Composting plant, Germany	Compost from green cuttings	65 mg kg^{-1} dry weight	-	-	-	Bläsing and Amelung, 2018
Composting plant, Germany	Compost from bio-waste	180 mg kg^{-1} dry weight	-	-	-	Bläsing and Amelung, 2018
Biogas plants, Germany	Digests from energy crops	0–11 items/kg	Fragments, fibers, spheres	1->5 mm	PP and PVC	Weithmann et al., 2018
Composting plant, Germany	8-mm and 15-mm sieved composts from bio-waste	20 and 24 items/kg	Fragments, fibers, spheres	1->5 mm	Styrene-based polymer, PE, PES, PP, PET, PVC	Weithmann et al., 2018
Anaerobic digestion plants, Germany	Bio-waste digests from households, food and drink industries	14–895 items/kg	Fragments, fibers, spheres	1->5 mm	Styrene-based polymer, PE, PES, PP, PET, PVC, cellulose-based polymer, PA, etc.	Weithmann et al., 2018
Composting plant, Guilin, Guangxi Province, South China	Raw sewage sludge composts	353.3 ± 97.0 items/kg	Flakes, fibers	< 0.2 -5 mm	PP, PP/PE, PET, PE, PB, EVA	Zhang et al., 2020
Composting plant, Guilin, Guangxi Province, South China	Finished sewage sludge composts	254.6 ± 84.1 items/kg	Flakes, fibers	< 0.2 -5 mm	PP, PP/PE, PET, PE, PB, EVA	Zhang et al., 2020

Location	Type	MP abundance	Shape	Size range	Polymer type	References
Herds in Murcia, Southeast Spain	Sheep feces	997 ± 971 items/kg	-	-	-	Beriot et al., 2021
Pig farm in Yingtan, Jiangxi Province, Southeast China	Pig manure	1250 ± 640 items/kg	Fibers, fragments, films	< 0.5 -5 mm	PES, PP, PE, and rayon	Yang et al., 2021

3.2 Characteristics of MPs in Different Organic Fertilizers

3.2.1 Size

As shown in Fig. 2 and Table S4, the size distribution of MPs in three types of commercial organic fertilizers and farm composts was similar and generally the contribution of MP fraction was inversely proportional to particle size. Approximately 54.0% of the total MPs were less than 1 mm, followed by the MPs in size range of 1–3 mm (average 35.2%), 3–5 mm (average 7.8%), and > 5 mm (average 3.0%). The majority of MPs (89.2%) were less than 3 mm, and the MPs with smaller size (< 1 mm) were especially predominant in APOFs (62.8%) and farm composts (60.7%). Our results were essentially consistent with the those observed in pig manure (Yang et al., 2021) and dewatered sewage sludge samples (Zhang et al., 2020). Yang et al. (2021) found that the MPs with size of < 3 mm accounted for 93.5% and 79.2% of the total MPs in pig manure and long-term manured soils, respectively; while for the MPs with size < 1 mm, those figures were 36.8% and 54.4%, respectively. The results implied that the high content of small-sized MPs may exert non-negligible influence on soil ecosystems, since they were more labile to be transported and readily ingested by soil organisms (Huerta Lwanga et al., 2017; Zhang et al., 2020; Yu et al., 2021).

3.2.2 Morphotype

As shown in Fig. 3, Fig. 4a, and Table S4, the MPs retained in the commercial organic fertilizers and farm composts were largely composed of fibers, fragments, and films, which accounted on average for 54.1%, 22.0%, and 18.9%, respectively. Pellet-like MPs contributed only 5.0% to the total, indicating that the MPs in the samples were mainly secondary MPs rather than primary MPs (Song et al., 2017; Pérez-Guevara et al., 2021). Moreover, the proportion of fiber-like MPs followed this sequence: FC (average 75.3%) > POF (average 65.9%) > APOF (average 52.1%) > AOF (average 49.9%), while the contributions of the other three shapes of MPs were in the opposite order. This suggested that plant-derived materials contained more fiber-like plastics than animal manures, probably because plant residues were under long-term exposure to the dispersed plastics in the environment where the fibers could be largely generated from textile weathering and washing, and the degradation of agricultural plastic products (Mahon et al., 2017; Chen et al., 2020; Zhang et al., 2020). Our results were consistent with the those observed in animal feces (Pérez-

Guevara et al., 2021). However, Weithmann et al. (2018) found that the majority of MPs were fragments (75–100%) and fibers only accounted for 0–8% of total MPs in the organic fertilizers derived from household waste, energy crop, and commercial biowaste. The results were different from ours, likely because only the MPs larger than 1 mm had been considered in their study (Weithmann et al., 2018).

3.2.3 Color

MPs in the commercial organic fertilizers and farm composts had a wide range of colors, including black (40.7%), red (17.7%), blue (11.3%), white (11.1%), yellow (10.4%), transparent (6.9%), and green (1.9%) (Fig. 4b and Table S5), indicating that the MPs came from diverse sources (Yu et al., 2021). Yang et al. (2021) also found the similar color characteristics in pig manure, in which black (32.8%) and blue (27.2%) were dominant colors. Moreover, a higher proportion of transparent pellet-like MPs was found in manure-based fertilizers (Fig. 4). This type of MPs was usually found in domestic sewage (Cheung and Fok, 2017; Chen et al., 2020) and soils (Chen et al., 2020; Yu et al, 2021) due to the wide use in personal care and cosmetic products and industrial abrasives. Animals may uptake these plastic residues from soil surface or water bodies and thereafter the MPs were accumulated in the feces (Huerta Lwanga et al., 2017; Pérez-Guevara et al., 2021).

3.2.4 Polymer type

Among the 114 selected MPs, about half of them were ambiguous due to the low similarity rates to the standard substances (Figure S2). This may attribute to the colored pigments, additives, or organic residues covered on the MPs or the ageing of MPs (Lenz et al., 2015; Imhof et al., 2016; Schymanski et al., 2018; Yan et al., 2020). Moreover, the spectra of some MPs could be changed during the digestion of Fenton’s reagent, such as PA (Yan et al., 2020). Finally, four MP polymer types were identified, including PP, PE, PVC, and PET (Fig. 5 and Fig. 6), which were the most common polymer types observed in animal feces (Pérez-Guevara et al., 2021; Yang et al., 2021) and organic fertilizers (Weithmann et al., 2018) (Table 2).

Among the identified MPs, PP (average 26.5%) and PE (average 18.7%) were more abundant than PET (average 6.5%) and PVC (average 5.2%) (Fig. 6). Moreover, the PP and the PE polymers were mainly films and fibers, while most of the PVC and the PET polymers were fragments and fibers. PP and PE are mainly used for food and drink packaging in daily life, and they are also the most widely used plastic types in agriculture, such as mulches, bale twines, containers, and fertilizer bags, etc. (PlasticsEurope, 2019; Chen et al., 2020; Zhang et al., 2020). PET is often used for drink bottles (Schymanski et al., 2018), while PVC has a wide range of applications in the materials for building and construction (PlasticsEurope, 2019). Therefore, the MPs in our organic fertilizers may come from both agricultural activities during the raw material production and their transportation and processing environment.

3.3 Environmental Concerns

The application of organic fertilizer has been believed to be an important pollution source of MPs in agricultural soils. Surprisingly, the detailed quantitative and qualitative data of MPs in organic fertilizers was rarely reported (Table 2). This study confirmed that a large number of MPs were accumulated in commercial organic fertilizers and farm composts, and the majority of the MPs were less than 1mm. In China, more than 11 million tons of commercial organic fertilizers were produced in 2015 (Tian et al., 2018). Based on the average MP content in commercial organic fertilizers we measured, a MP flux of 1.0×10^{14} items/year was estimated to be potentially introduced into the environment, which was close to the estimated emission of MPs (1.56×10^{14} items/year) from WWTP sewage sludge in China (Li et al., 2018). Moreover, according to the recommended application doses of organic fertilizer, which varied from 2.25 t/ha/year to 5.1 t/ha/year for different crops (Du et al., 2020), $2.1 \times 10^7 - 4.7 \times 10^7$ items/ha of MPs might be transported into agricultural soils each year. Taking 10-cm topsoil (ρ = 1.2 g/cm^3) into consideration, the application of organic fertilizer could result in increasing MP contamination in soil by 17.5 ~ 39.1 items/kg/year. Although the exploration based on the MP contents in small sampling volume may cause increased uncertainties in our results, this study could at least provide a detailed assessment of MP accumulation in organic fertilizers and emphasize that more attention should be paid to their potential environmental risk.

In particular, our results also highlighted the effects of raw materials and treatment processes on MP loads and characteristics in organic fertilizers. The results suggested that the selection of mixed raw materials of plant-derived materials and animal manures and the mechanical processing within standardized manufacturing environment can significantly reduce the MP loads in the end products. However, most countries have not yet regulated the plastic contents in organic fertilizers, except Germany, which allows up to 0.1% weight of plastics (Weithmann et al., 2018). Therefore, the standards, concerning the limiting amounts of plastics both in raw materials and end products and necessary treatment processes, are required for the manufacture of organic fertilizers, so as to control the MP pollution. Moreover, our findings still need to be further confirmed by controlled experiments in the future.

4. Conclusions

Our study confirmed that MPs were abundant in commercial organic fertilizers and farm composts. The majority of MPs were less than 3 mm, and the MPs with size of < 1 mm were especially predominant, implying the potential risk of MP contamination in terrestrial ecosystem through the application of organic fertilizers. The variations in MP abundances and characteristics in different types of organic fertilizers suggested the mixing with mechanically treated plant-derived materials within standardized manufacturing environment can significantly reduce the MP loads in the end products. Therefore, the standards regulating plastic contents both in in raw materials and end products and the treatment processes should be established in the future.

Declarations

Supplementary Materials

Detailed information of the recovery test (Table S1-S2, Figure S1) and the characteristics of MPs (abundance, size distribution, morphotype, color, and polymer type) in each organic fertilizer sample (Table S3-S5, Figure S2).

Ethical Approval

Not applicable.

Consent to Participate

Not applicable.

Consent to Publish

Not applicable.

Authors Contributions

Jieru Xu, Aiping Yang, Yu Yan, Yuqi Xu, Minyi Tang, Penghui Li: material preparation, data collection and analysis; **Lanfeng Zhao:** methodology and validation; **Xinming Zhang:** revision of the article; **Zongling Ren:** funding acquisition, conceptualization, and writing the original draft.

Funding

This research was supported by the Science and Technology Foundation of Guangzhou (201903010026), Natural Science Foundation of China (41877361 and 41811530277), and Natural Science Foundation of Guangdong Province, China (2021A1515011283).

Competing Interests

The authors declare no competing interests.

Availability of data and materials

The detailed data used in this manuscript is provided in the supplementary information. If further information is required, it will be provided on request.

References

1. Afonso S, Arrobas M, Pereira EL, Rodrigues M (2021) Recycling nutrient-rich hop leaves by composting with wheat straw and farmyard manure in suitable mixtures. J Environ Manage 284:112105
2. Beriot N, Peek J, Zornoza R, Geissen V, Huerta Lwanga E (2021) Low density-microplastics detected in sheep faeces and soil: A case study from the intensive vegetable farming in Southeast Spain. Sci Total Environ 755:142653

3. Bläsing M, Amelung W (2018) Plastics in soils: Analytical methods and possible sources. Sci Total Environ 612:422–435
4. Chen Y, Leng Y, Liu X, Wang J (2020) Microplastic pollution in vegetable farmlands of suburb Wuhan, centra China. Environ Pollut 257:113449
5. Cheung PK, Fok L (2017) Characterisation of plastic microbeads in facial scrubs and their estimated emissions in Mainland China. Water Res 122:53–61
6. Du W, Tang S, Wang H (2020) The status of organic fertilizer industry and organic fertilizer resources in China. Soil and Fertilizer Sciences in China. 3: 210–219. (In Chinese)
7. He D, Luo Y, Lu S, Liu M, Song Y, Lei L (2018) Microplastics in soils: Analytical methods, pollution characteristics and ecological risks. Trends Anal Chem 109:163–172
8. Hidalgo-Ruz V, Gutow L, Thompson RC, Thiel M (2012) Microplastics in the marine environment: A review of the methods used for identification and quantification. Environ Sci Technol 46:3060–3075
9. Huerta Lwanga E, Mendoza Vega J, Ku Quej V, Chi L, Chi C, Segura E, Gertsen G, Salánki H, van der Ploeg T, Koelmans M, Geissen AA (2017) V. Field evidence for transfer of plastic debris along a terrestrial food chain. *Sci. Rep.* 7:14071
10. Hurley RR, Lusher AL, Olsen M, Nizzetto L (2018) Validation of a method for extracting microplastics from complex, organic -rich, environmental matrices. Environ Sci Technol 52:7409–7417
11. Hurley RR, Nizzetto L (2018) Fate and occurrence of micro(nano)plastics in soils: Knowledge gaps and possible risks. Curr Opin Environ Sci Health 1:6–11
12. Imhof HK, Laforsch C, Wiesheu AC, Schmid J, Anger PM, Niessner R, Ivleva NP (2016) Pigments and plastic in limnetic ecosystems: A qualitative and quantitative study on microparticles of different size classes. Water Res 96:64–74
13. Lenz R, Enders K, Stedmon CA, Mackenzie DMA, Nielsen TG (2015) A critical assessment of visual identification of marine microplastic using Raman spectroscopy for analysis improvement. Mar Pollut Bull 100:82–91
14. Li P, Kong D, Zhang H, Xu L, Li C, Wu M, Jiao J, Li D, Xu L, Li H, Hu F (2021) Different regulation of soil structure and resource chemistry under animal- and plant-derived organic fertilizers changed soil bacterial communities. Appl Soil Ecol 165:104020
15. Li X, Chen L, Mei Q, Dong B, Dai X, Ding G, Zeng EY (2018) Microplastics in sewage sludge from the wastewater treatment plants in China. Water Res 142:75–85
16. Liu H, Wang Z, Nghiem LD, Gao L, Zamyadi A, Zhang Z, Sun J, Wang Q (2021) Solid-embedded microplastics from sewage sludge to agricultural soils: Detection, occurrence, and impacts. ACS ES&T Water 1:1322–1333
17. Mahon AM, O'Connell B, Healy MG, O'Connor I, Officer R, Nash R, Morrison L (2017) Microplastics in sewage sludge: Effects of treatment. Environ Sci Technol 51:810–818
18. MOA (Ministry of Agriculture and Rural Affairs of the People's Republic of China) (2012) http://www.moa.gov.cn/govpublic/CWS/201206/t20120606_2751150.htm

19. MOA (Ministry of Agriculture and Rural Affairs of the People's Republic of China) (2017) http://www.moa.gov.cn/govpublic/ZZYGLS/201702/t20170210_5472878.htm
20. Munno K, De Frond H, O'Donnell B, Rochman CM (2020) Increasing the accessibility for characterizing microplastics: Introducing new application-based and spectral libraries of plastic particles (SLoPP and SLoPP-E). Anal Chem 92:2443–2451
21. Nguyen B, Claveau-Mallet D, Hernandez LM, Xu EG, Farner JM, Tufenkji N (2019) Separation and analysis of microplastics and nanoplastics in complex environmental samples. Acc Chem Res 52:858–866
22. Nuelle M-T, Dekiff JH, Remy D, Fries E (2014) A new analytical approach for monitoring microplastics in marine sediments. Environ Pollut 184:161–169
23. Okeke ES, Okoye CO, Atakpa EO, Ita RE, Nyaruaba R, Mgbechidinma CL, Akan OD (2022) Microplastics in agroecosystems-impacts on ecosystem functions and food chain. Resour Conserv Recy 177:105961
24. Pérez-Guevara F, Kutralam-Muniasamy G, Shrutic VC (2021) Critical review on microplastics in fecal matter: Research progress, analytical methods and future outlook. Sci Total Environ 778:146395
25. PlasticsEurope (2019) Plastics-the facts 2019: An analysis of European plastics production, demand and waste data. https://plasticseurope.org/wp-content/uploads/2021/10/2019-Plastics-the-facts.pdf
26. Schymanski D, Goldbeck C, Humpf H-U, Fürst P (2018) Analysis of microplastics in water by micro-Raman spectroscopy: Release of plastic particles from different packaging into mineral water. Water Res 129:154–162
27. Song YK, Hong SH, Jang M, Han GM, Jung SW, Shim WJ (2017) Combined Effects of UV Exposure Duration and Mechanical Abrasion on Microplastic Fragmentation by Polymer Type. Environ Sci Technol 51:4368–4376
28. Tian S, Guo H, Yao L, Gong Z, Dong L, Bian W, Luo J, Zhang Y (2018) Development analysis for fertilizer utilization of agricultural planting and animal wastes in China. Trans Chin Soc Agricultural Eng 34:123–131 (In Chinese)
29. von Sperber C, Lewandowski H, Tamburini F, Bernasconi SM, Amelung W, Frossard E (2016) Kinetics of enzyme-catalysed oxygen isotope exchange between phosphate and water revealed by Raman spectroscopy. J Raman Spectrosc 48:368–373
30. Weithmann N, Möller JN, Löder MGJ, Piehl S, Laforsch C, Ruth F (2018) Organic fertilizer as a vehicle for the entry of microplastic into the environment. Sci Adv 4:eaap8060
31. Yan Z, Zhao H, Zhao Y, Zhu Q, Qiao R, Ren H, Zhang Y (2020) An efficient method for extracting microplastics from feces of different species. J Hazard Mater 384:121489
32. Yang J, Li R, Zhou Q, Li L, Li Y, Tu C, Zhao X, Xiong K, Christie P, Luo Y (2021) Abundance and morphology of microplastics in an agricultural soil following long-term repeated application of pig manure. Environ Pollut 272:116928

33. Yi X, Yu L, Chang S, Yin C, Wang H, Zhang Z (2021) The effects of China's Organic-Substitute-Chemical-Fertilizer (OSCF) policy on greenhouse vegetable farmers. J Clean Prod 297:126677
34. Yu L, Zhang JD, Liu Y, Chen L, Tao S, Liu WX (2021) Distribution characteristics of microplastics in agricultural soils from the largest vegetable production base in China. Sci Total Environ 756:143860
35. Zhang L, Xie Y, Liu J, Zhong S, Qian Y, Gao P (2020) An overlooked entry pathway of microplastics into agricultural soils from application of sludge-based fertilizers. Environ Sci Technol 54:4248–4255
36. Zhu D, Chen Q-L, An X-L, Yang X-R, Christie P, Ke X, Wu L-H, Zhu Y-G (2018) Exposure of soil collembolans to microplastics perturbs their gut microbiota and alters their isotopic composition. Soil Biol Biochem 116:302–310

Figures

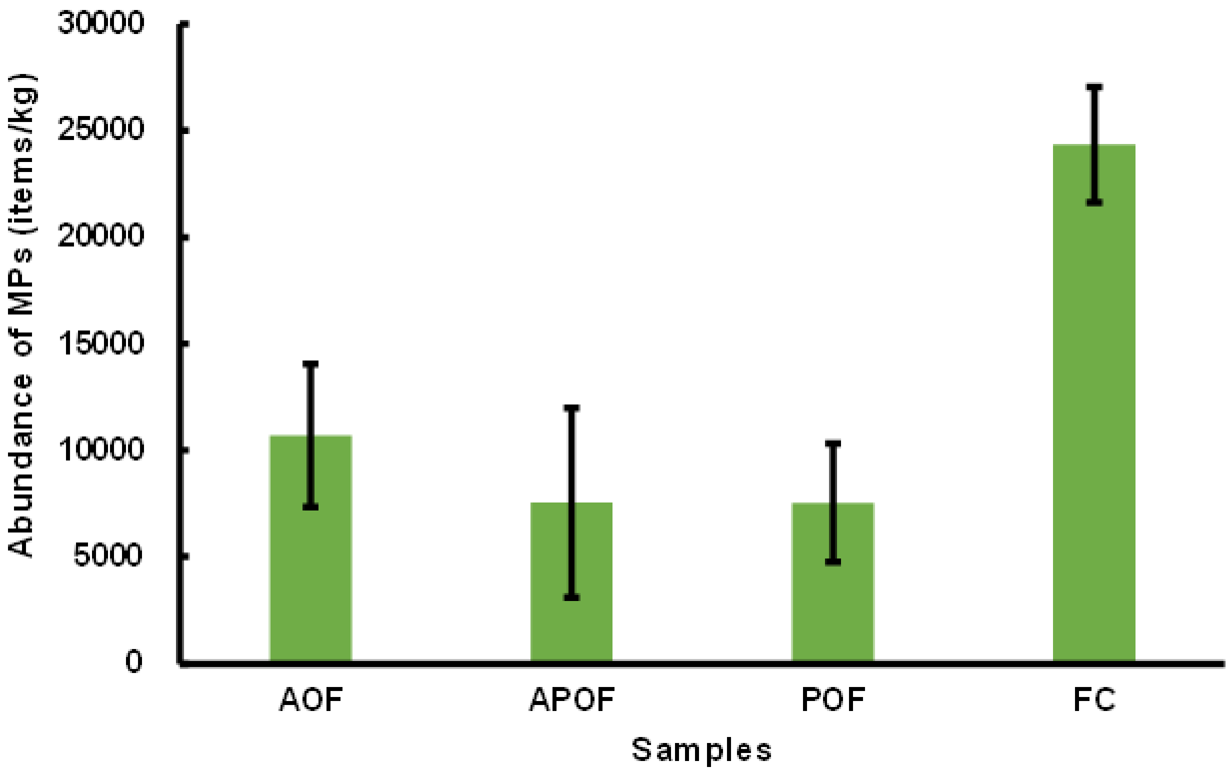

Figure 1

Average abundance of MPs observed in the animal-derived organic fertilizers (AOF, *n* = 11), organic fertilizers made from the mixture of plant- and animal-derived materials (APOF, *n* = 10), plant-derived organic fertilizers (POF, *n* = 2), and farm composts (FC, *n* = 2).

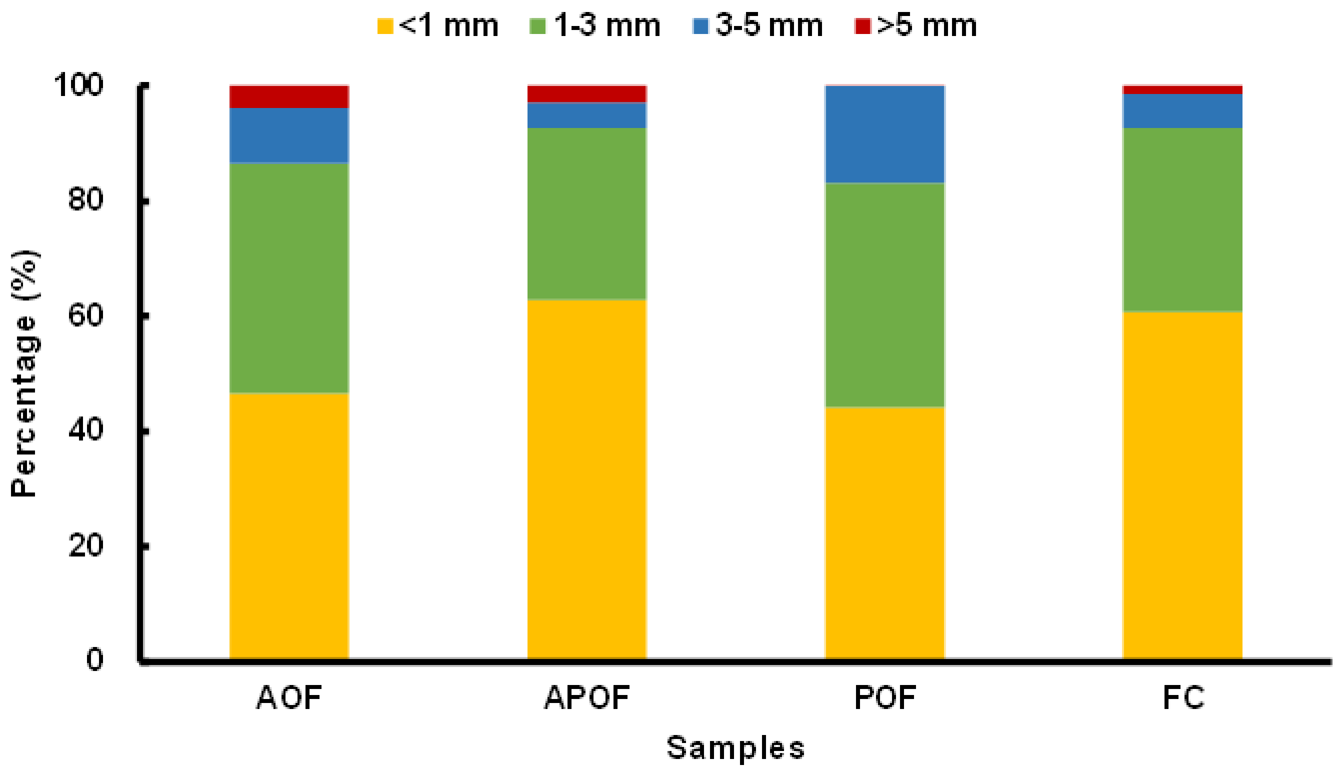

Figure 2

Size distribution of MPs observed in the animal-derived organic fertilizers (AOF, n = 11), organic fertilizers made from the mixture of plant- and animal-derived materials (APOF, n = 10), plant-derived organic fertilizers (POF, n = 2), and farm composts (FC, n = 2).

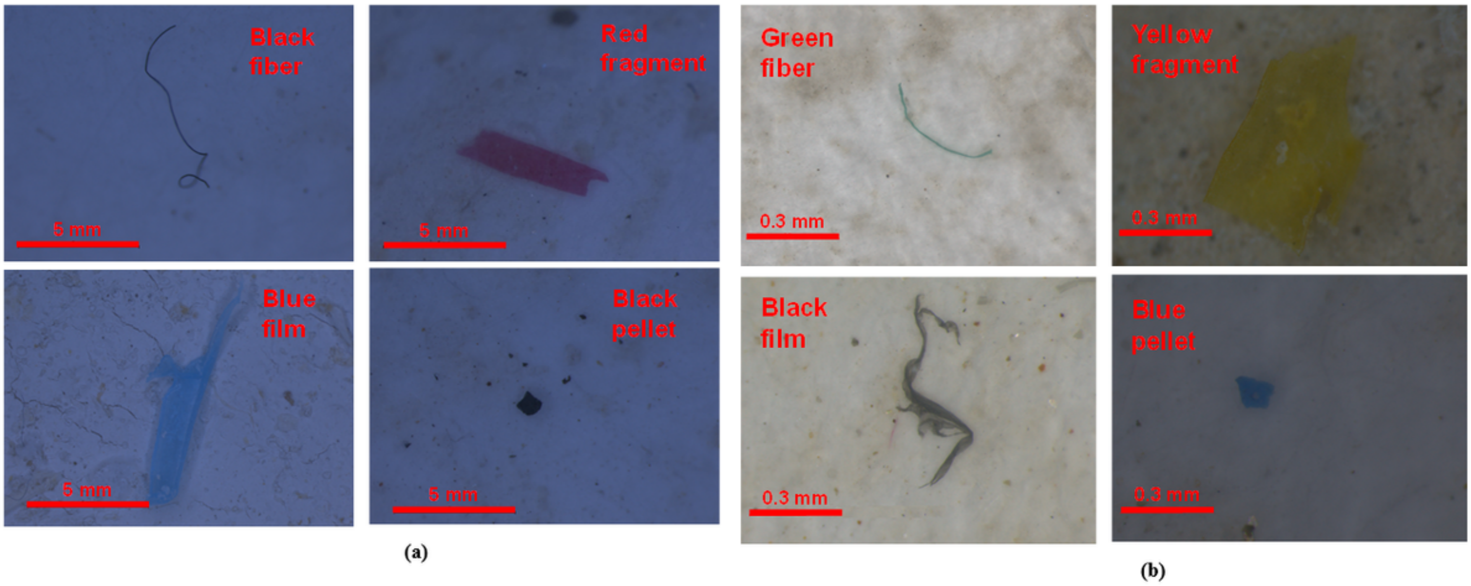

Figure 3

Stereomicrograph of visible (a) and small-sized (b) MPs extracted from the organic fertilizers.

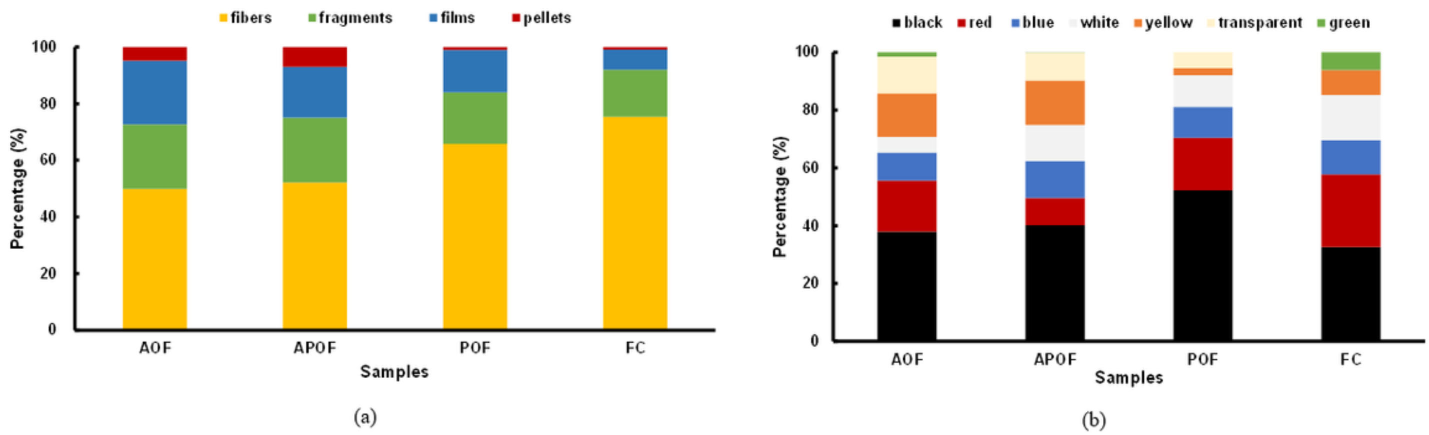

Figure 4

Relative proportions of shape (a) and color (b) of MPs observed in the animal-derived organic fertilizers (AOF, *n* = 11), organic fertilizers made from the mixture of plant- and animal-derived materials (APOF, *n* = 10), plant-derived organic fertilizers (POF, *n* = 2), and farm composts (FC, *n* = 2).

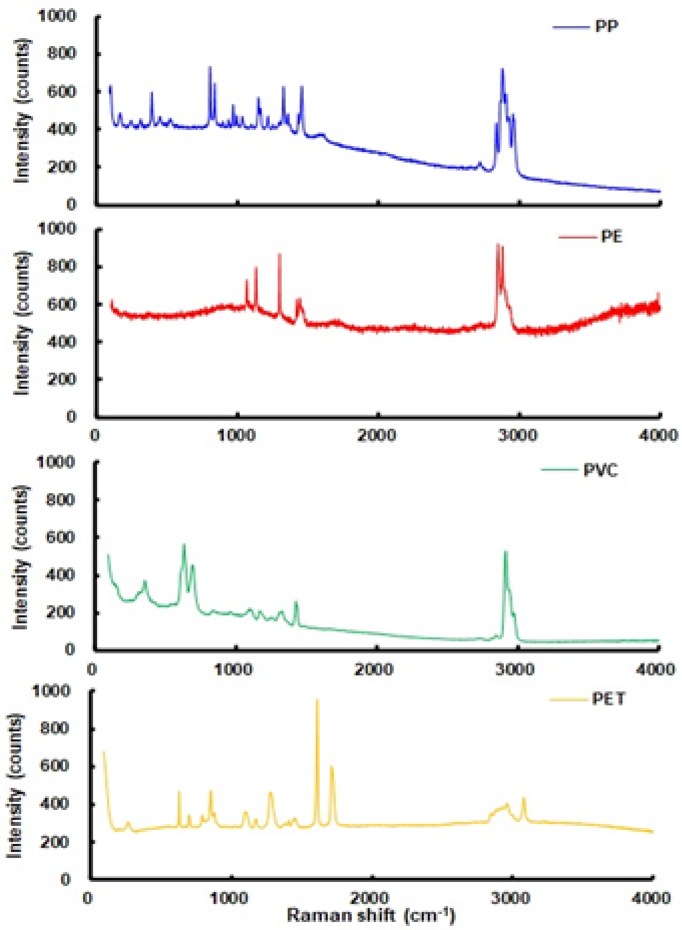

Figure 5

Raman spectra of four types of MPs, including PP, PE, PVC, and PET.

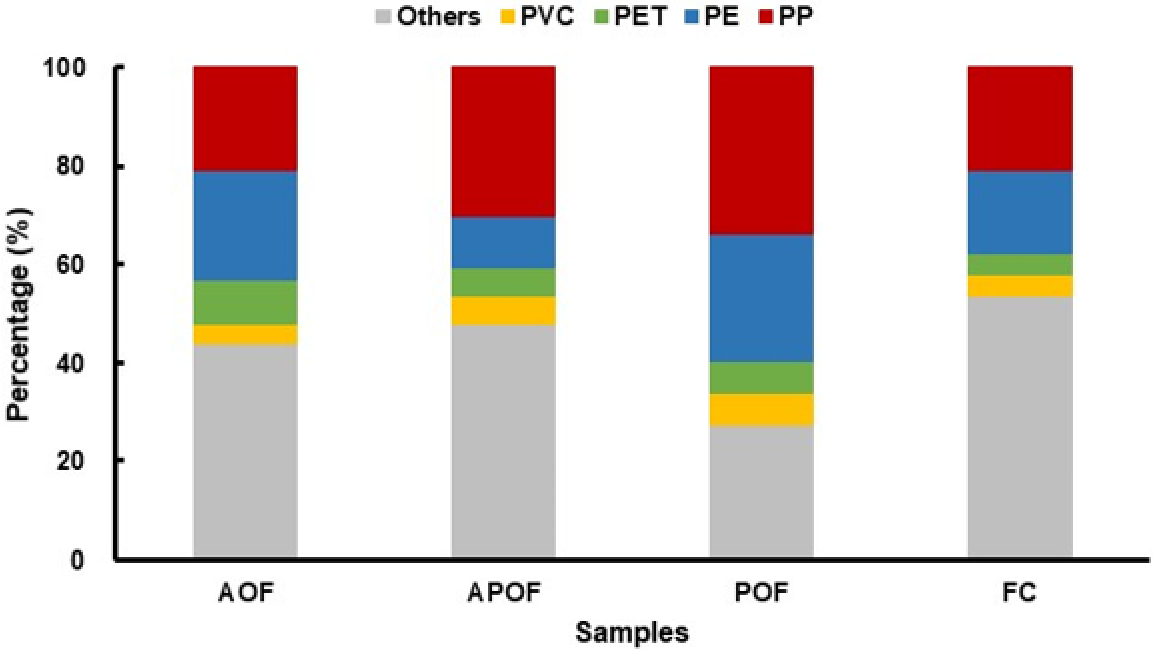

Figure 6

The distribution of polymer types among particles observed in the animal-derived organic fertilizers (AOF, *n* = 11), organic fertilizers made from the mixture of plant- and animal-derived materials (APOF, *n* = 10), plant-derived organic fertilizers (POF, *n* = 2), and farm composts (FC, *n* = 2).

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- XuetalSI.docx