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Influence of microplastic addition on glyphosate decay and soil microbial activities in Chinese loess soil☆

Xiaomei Yang [a, b, c], Célia P.M. Bento [b], Hao Chen [b], Hongming Zhang [b, d], Sha Xue [b, c, *], Esperanza Huerta Lwanga [b, e], Paul Zomer [f], Coen J. Ritsema [b], Violette Geissen [b]

[a] State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi, 712100, China
[b] Soil Physics and Land Management, Wageningen University & Research, P.O. Box 47, 6700 AA, Wageningen, the Netherlands
[c] State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Institute of Soil and Water Conservation, Northwest A&F University, Yangling, Shaanxi, 712100, China
[d] College of Information Engineering, Northwest A&F University, Yangling, Shaanxi, 712100, China
[e] Agroecología, El Colegio de la Frontera Sur, Unidad Campeche, Av Poligono S/n, Ciudad Industrial, Lerma, Campeche, Mexico
[f] Institute of Food Safety (RIKILT), Wageningen University & Research, P.O. Box 230, 6700 AE, Wageningen, the Netherlands

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ABSTRACT

The intensive use of pesticide and plastic mulches has considerably enhanced crop growth and yield. Pesticide residues and plastic debris, however, have caused serious environmental problems. This study investigated the effects of the commonly used herbicide glyphosate and micrometre-sized plastic debris, referred as microplastics, on glyphosate decay and soil microbial activities in Chinese loess soil by a microcosm experiment over 30 days incubation. Results showed that glyphosate decay was gradual and followed a single first-order decay kinetics model. In different treatments (with/without microplastic addition), glyphosate showed similar half-lives (32.8 days). The soil content of aminomethylphosphonic acid (AMPA), the main metabolite of glyphosate, steadily increased without reaching plateau and declining phases throughout the experiment. Soil microbial respiration significantly changed throughout the entirety of the experiment, particularly in the treatments with higher microplastic addition. The dynamics of soil β-glucosidase, urease and phosphatase varied, especially in the treatments with high microplastic addition. Particles that were considerably smaller than the initially added microplastic particles were observed after 30 days incubation. This result thus implied that microplastic would hardly affect glyphosate decay but smaller plastic particles accumulated in soils which potentially threaten soil quality would be further concerned especially in the regions with intensive plastic mulching application.

1. Introduction

With remarkable versatilities and benefits (Andrady and Neal, 2009), plastic has been enormously used in industries, agriculture and human daily life, as a key geological indicator of the Anthropocene Era (Zalasiewicz et al., 2016). The global annual production of plastic materials is up to 322 million tonnes (PlasticsEurope, 2016), equivalent to 46 kg of plastic produced annually for every individual of the 7.3 billion people. Plastic debris however, has become a severe environmental problem due to its high disposability, high durability, and low recovery of plastic waste materials (Comăniţă et al., 2016; Hammer et al., 2012; Law, 2017).

The most commonly used plastic materials are polyethylene, polypropylene, polyvinyl chloride, polystyrene and polyethylene terephthalate, with the densities ranging from 0.9 to 1.28 g cm^{-3} (Nuelle et al., 2014). Although plastics are recalcitrant in the environment, the slow degradation process can be accelerated under certain conditions (Bhardwaj et al., 2012; Singh and Sharma, 2008), resulting in the release of adsorbed toxic compounds into the surroundings (Koelmans et al., 2013). Studies showed that phthalate esters, widely used as plasticizers, are

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* Corresponding author. State Key Laboratory of Soil Erosion and Dryland arming on the Loess Plateau, Institute of Soil and Water Conservation, Northwest A&F University, Yangling, Shaanxi, 712100, China.
E-mail address: xuesha100@163.com (S. Xue).

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frequently detected in soils (Li et al., 2016), sediment (Adeogun et al., 2015), and water bodies (Driedger et al., 2015). With the effects of environment, including physical forces and microbial degradation, plastic particle size can be changed and small plastic particles can float, settle, and be transported by wind or raindrop-induced erosion to downstream land, lakes, rivers, estuaries and coastal areas (Gil-Delgado et al., 2017; Jambeck et al., 2015; Law, 2017; Mason et al., 2016).

With the increasing use of plastic mulch in agriculture, plastic residues in soil have become a severe challenge for long-term farming and environmental protection (Steinmetz et al., 2016). Plastic film mulching can maintain and conserve soil temperature and moisture (Wu et al., 2017) but can induce different responses in soil physicochemical properties (Cuello et al., 2015; Wang et al., 2017; Zhang et al., 2017). Wang et al. (2017) found that the continuous use of plastic mulch increased soil aggregation, particularly the formation of macroaggregates (>0.25 mm), by 16%–28% but soil pH declined by 0.19–0.54 units. Soil microbial carbon and nitrogen, enzyme activities and microbial diversity decreased significantly with increasing accumulation of plastic residues (Farmer et al., 2017; Moreno and Moreno, 2008; Wang et al., 2011). Furthermore, biodegradable and non-biodegradable plastic debris can also be digested as a non-target feeder by earthworms (Huerta et al., 2016; Rillig et al., 2017b) and soil microbes (Koitabashi et al., 2016; Wang et al., 2011). This leads to potential environmental risks associated to smaller plastic particles (<5 mm in size), referred as microplastics, leaching into deeper soil layers (Huerta Lwanga et al., 2016; Rillig, 2012). Nizzetto et al. (2016) reported that farmland is suffering from microplastics contamination that mainly originates from sewage sludge, household and laundry dust and nearby industrial facilities. In addition, small plastic particles are prone to absorbing and accumulating pesticides and other biocides in the soil, such as cypermethrin (Emden and Hadley, 2011; Ramos et al., 2015). However, plastic debris in soil enhanced soil activity of fluorescein diacetate hydrolase and increased the nutrient contents in soil dissolved organic matter (Liu et al., 2017). These new vectors, macro/microplastics, can be transported or leached together with soil particles, thus threatening on-site soil and water quality or off-site ecosystems by enriching agrochemical concentrations (Lee et al., 2014; Woodall et al., 2014).

Given the increasing use of plastic products, more attention should be paid to the effects of cumulative plastic residues, especially microplastics, on soil quality and on agrochemicals behaviour. Many studies have investigated the occurrence, concentration and impacts of microplastics in aquatic organisms (Galloway and Lewis, 2016; Sussarellu et al., 2016), edible products (Yang et al., 2015a) and fresh water bodies (Wang et al., 2016b) but not in the soil matrix together with pesticide (Lenz et al., 2016). Thus, in the present study, the widely used herbicides glyphosate (Yang et al., 2014) and microplastics were taken into account and a pot experiment to study the influence of microplastic addition on glyphosate decay and on soil microbial activity was conducted. The main objectives of this study are: 1) to study the effects of microplastic addition on the degradation behaviour of glyphosate and the consequent formation of its main metabolite aminomethylphosphonic acid (AMPA); 2) to analyse soil enzyme activities under different microplastic and glyphosate additions; and 3) to study the changes in the particle sizes of microplastics before and after incubation. The results of this study may provide prime and direct evidence for the effects of microplastic accumulation on glyphosate fate in soil and responses of indicator for soil quality.

2. Materials and methods

2.1. Experimental design

2.1.1. Soil and facilities

Soil was collected from the topsoil of a farm in Ansai (109°32′ N, 36°87′ W) in the Loess Plateau, North Shaanxi Province, China. This area is in a temperate climatic zone with continental semi-arid monsoon climate, an average annual temperature of 8.8 °C, average annual precipitation of 505.3 mm and 157 days of frost-free season. The collected soil was homogenized, air-dried and sieved to a particle size of 2 mm. The soil was composed of 18.4% clay (<0.002 mm), 25.0% silt (0.002–0.02 mm) and 55.9% sand (0.02–2 mm) and had a pH (H_2O) of 8.6 and organic matter content of 5.1 g kg^{-1}. The soil had a total nitrogen content of 0.86 g kg^{-1}, ammonium nitrogen content of 3.4 mg kg^{-1}, nitrate nitrogen content of 1.95 mg kg^{-1}, total phosphorus content of 0.57 g kg^{-1} and available phosphorus content of 5.0 mg kg^{-1}. The content of glyphosate and AMPA in the selected soil was 0.04 μg g^{-1} and 0.09 μg g^{-1}, respectively, and microplastic content was less than 0.1% in each gram air-dried soil. The experiment was conducted in a climate chamber at the State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Institute of Soil and Water Conservation, China. Temperature and humidity were controlled through an automatic control panel. Light was manually controlled in a 16 h/8 h on/off cycle.

2.1.2. Preparation of glyphosate solutions

Glyphosate solutions were prepared by dissolving glyphosate (98% purity, purchased from Dr. Ehrenstorfer, Germany) in deionized water in plastic containers. The solutions had a final concentration of 0.46 g l^{-1} and 0.92 g L^{-1}, equivalent to 3.6 kg a.i. ha^{-1} and 7.2 kg a.i. ha^{-1}, respectively, and to a glyphosate content in pure dry soil of 11.5 μg g^{-1} and 23.0 μg g^{-1}, respectively. The glyphosate solutions were stored at 4 °C until use.

2.1.3. Experiment setup

A series of experiments was conducted to test the effects of microplastic accumulation on glyphosate decay and on soil microbial activities in Chinese loess soil under simulated growing season conditions. Analytical grade homopolymer polypropylene (materials for plastic film or products) powder was used as the microplastic and was purchased from Youngling-TECH Company (Beijing, China). The material had 0.91 g cm^{-3} density, 3.6 g min^{-1} melt flow rate and a particle size of <250 μm. Two glyphosate application rates (3.6 kg a.i. ha^{-1} (G1) and 7.2 kg a.i. ha^{-1} (G2)) and two levels of microplastic addition (7% (M1) and 28% (M2), w/w) were used as treatments. The applied glyphosate doses were selected on the basis of the local glyphosate application rates (Yang et al., 2015b). The microplastic contents were selected on the basis on the results of a study that simulated the hotspots of plastic debris in the field (Huerta Lwanga et al., 2016). Soil moisture was set to 10% (approximately 60% of soil field capacity, w:w) and monitored on a daily basis by deionized water. The experiment was conducted as a pot experiment in sealed 330 mL PVC plastic pots in a climate chamber at 28 °C and a relative air humidity of 80%. Given that the soil was air-dried, the soil was pre-incubated for 1 week to re-establish microbial metabolism without adding microplastic and glyphosate. A total of 9 treatment combinations were utilized: control (only soil; CK), G1 (3.6 kg ha^{-1} glyphosate), M1 (7% microplastics); M2 (28% microplastics), M1G1 (7% microplastics, 3.6 kg ha^{-1} glyphosate), M2G1 (28% microplastics, 3.6 kg ha^{-1} glyphosate), G2 (7.2 kg ha^{-1} glyphosate), M1G2 (7% microplastics,

7.2 kg ha^{-1} glyphosate) and M2G2 (28% microplastics, 7.2 kg ha^{-1} glyphosate) (Table S1). Each treatment was applied in triplicate.

2.2. Microplastics/glyphosate application and sampling

Microplastics were added to 200 g soil (dry weight) in accordance with the desired contents (see section 2.1.3) after 7-day incubation. The soil–microplastic was evenly mixed and slightly paved by a soil compactor. After compaction soil, 5 mL of glyphosate solution was evenly sprayed on the soil surface of each pot in accordance with the desired concentrations (see section 2.1.2). The sprayed soil was then mixed using a plastic stick. A small plastic soil compactor was used to compact the soil by free gravity falling as mentioned. Concerning the temperature and incubation condition, the pots were covered with porous plastic film secured by rubber bands. The experiment was conducted for 30 days after mciroplastic and glyphosate application.

Soil samples were collected on the day (D0) of glyphosate application and 1 (D1), 3 (D3), 7 (D7), 14 (D14) and 30 (D30) days after glyphosate application. All soil samples were divided into three subsample groups. One group was used for glyphosate/AMPA detection and stored at −20 °C until analysis. Another group was used for microplastic residue testing. The third group was used to test soil microbial activities.

2.3. Sample analysis

2.3.1. Glyphosate/AMPA analysis

Glyphosate/AMPA contents were detected in each soil sample by high-performance liquid chromatography tandem mass spectrometry in accordance with the methodology described by Yang et al. (2015b).

2.3.2. Microplastics determination

The quantity and particle size of microplastic residues in the soil at each sampling day were determined in accordance with the method developed by Huerta Lwanga et al. (2016). Briefly, 10 g of soil was oven-dried at 40 °C and sieved through sieves of 5 different diameters (250 μm, 125 μm, 100 μm, 63 μm, 50 μm). Then, the sieved soil was transferred into 50 mL cups. Millipore-purified water was added to the cups, causing the microplastic particles to float. Each soil sample was subjected to floating 3–5 times. Then, the separation of the microplastics from soil was confirmed through visual inspection using a stereoscope (Leica wild M3C, Type S, simple light). The samples were then dried, weighted and clustered in the following particle size groups: <50 μm, 50–63 μm, 63–100 μm, 100–125 μm, 125–250 μm.

2.3.3. Microbiology activity measurement (respiration and enzymatic)

Soil basal respiration and substrate-induced respiration were determined using the unit of ppm CO_2 g^{-1} soil h^{-1} (Menyailo et al., 2003), and the procedures have been described in a previous study (Xue et al., 2017). Soil enzyme activity assays, such as β-glucosidase, urease, phosphatase, was conducted. Briefly, β-glucosidase was determined using 1 g of fresh soil, 125 mL of 50 mM sodium acetate buffer at pH 6.0 homogenizing for 2 min. Then, 50 μL (200 μM substrate) of fluorometric substrate solution and 50 μL of soil slurry was mixed in a microplate and incubated for 1 h at 37 °C. After incubation, 10 μL of 1.0 M NaOH was added to stop the reaction. Fluorescence was measured using a microplate fluorometer by SpectraMax with 365 nm excitation and 450 nm emission filters. Each assay microplate contained two columns of blanks for the correction of background fluorescence in the substrate. β-glucosidase activities were expressed in μmol glucose g^{-1} soil h^{-1}. Urease activity was determined as following steps. 1 mL of toluene was added to 3 g of fresh soil. After 15 min, 10 mL of 10% urea solution were added. Then the samples were incubated at 37 °C for 24 h, diluted to 50 mL with distilled water and filtered. Then, 0.5 mL of the extract was treated with 2 mL of sodium phenol solution (100 mL of 6.6 M phenol solution and 100 mL of 6.8 M NaOH) and 1.5 mL of 0.9% sodium hypochlorite solution. The released ammonium was colorimetrically quantified by spectrophotometer (Hitachi, UV2800) at 578 nm. Urease activity was expressed in μmol ammonium g^{-1} soil h^{-1}. Phosphatase activity was determined using 1 g of fresh soil, 50 mL of 50 mM acetate buffer and 200 mM 4-methylumbelliferyl. The samples were incubated in the dark at 25 °C for 4 h. Fluorescence was quantified using a microplate fluorometer (Molecular Devices SpectraMax M2 Multi-Mode Microplate Reader, USA) with 365 nm excitation and 450 nm emission filters. The results were expressed in μmol phosphatase g^{-1} soil h^{-1}. All essays used in our experiment mentioned above were purchased from Sigma-Aldrich (USA).

2.4. Data analysis

The means and standard deviations for all microplastic residue, glyphosate and AMPA rate comparing with initial application were calculated. Microplastic residues were calculated on the basis of floating weight and the initial added amount. Glyphosate and AMPA were corrected on the basis of residue in per gram soil. The model parameters for the decay kinetics of glyphosate and AMPA were estimated using ModelMaker 4 (A.P. Benson) (Bento et al., 2016). For model estimation, all glyphosate and AMPA concentrations were converted to the percentage of initially added glyphosate. The procedure to determine and select the kinetic model that best describes the decay of glyphosate and formation of AMPA was as described by Bento et al. (2016). The single first-order (SFO, Eq.[1]) kinetic model for glyphosate decay and AMPA formation was considered:

$$\text{SFO:} C_t = C_0 e^{-kt} \quad (1)$$

where C_t is the glyphosate content at time t, C_0 is the initial glyphosate content ($t = 0$), and k is the degradation rate constant. The life-time of glyphosate, DT_{50} (the half-life time) and DT_{90} (the time for 90% of the initially applied glyphosate to disappear from soil), hence, were calculated on the basis of SFO.

The differences in glyphosate and AMPA detection rate, soil enzyme activities (β-glucosidase, urease, phosphatase) and soil microbial respiration (basal respiration and substrate-induced respiration) among samples taken on different days ($p < 0.05$) were compared using one-way analysis of variance with least significant difference (LSD) tests. LSD tests were also conducted to compare the significant differences among treatments sampled on the same incubation day ($p < 0.05$). Statistical analyses were performed using SPSS 22.0.

3. Results

3.1. Glyphosate/AMPA residues and glyphosate decay

Glyphosate and AMPA residues were detected in all samples under glyphosate treatment (G1, M1G1, M2G1, G2, M1G2 and M2G2). Comparing with initial glyphosate application rate, the detected rate of glyphosate significantly declined during the whole observation days in all treatments ($p < 0.05$) (Table 1a). Although two levels of glyphosate were applied, no significant difference was observed among different levels of micropalstic addition. Accordingly, AMPA was detected in all soil samples where glyphosate was

Table 1a
Detection rate of glyphosate in soil of different treatments during the incubation period.

Treatment	Detection rate of glyphosate in different sampling day					
	D0	D1	D3	D7	D14	D30
G1	0.99 ± 0.05 a	0.95 ± 0.05 a	0.90 ± 0.01 a	0.76 ± 0.01 b	0.66 ± 0.02 c	0.56 ± 0.03 d
M1G1	0.92 ± 0.08 a	0.81 ± 0.05 b	0.76 ± 0.01 b	0.65 ± 0.02 c	0.58 ± 0.08 c	0.46 ± 0.01 d
M2G1	0.95 ± 0.07 a	0.84 ± 0.04 b	0.81 ± 0.02 bc	0.75 ± 0.03 c	0.69 ± 0.05 c	0.51 ± 0.03 d
G2	0.95 ± 0.01 a	0.87 ± 0.02 b	0.86 ± 0.05 c	0.72 ± 0.02 d	0.67 ± 0.04 d	0.53 ± 0.08 e
M1G2	0.95 ± 0.04 a	0.85 ± 0.01 b	0.75 ± 0.01 c	0.65 ± 0.02 d	0.61 ± 0.03 e	0.53 ± 0.04 e
M2G2	0.93 ± 0.04 a	0.91 ± 0.03 a	0.76 ± 0.02 b	0.69 ± 0.04 c	0.61 ± 0.03 d	0.50 ± 0.04 e

Different lowercase letters within the same row mean significant differences on detection rate of glyphosate during the incubation days in the same treatment ($p < 0.05$).

applied and steadily increased throughout the entire experimental period (Table 1b). Similarly, there was no significant difference detected among the treatments with different levels of microplastic addition.

The glyphosate decay curves for the different treatments were estimated from the amounts of the glyphosate residues per treatment (Fig. 1). The results showed that glyphosate gradually decayed under the different treatments with microplastic addition during incubation and presented similar degradation rates at the beginning of incubation. Accordingly, AMPA content steadily increased without reaching the maximum concentration, or the plateau phase of glyphosate degradation, throughout the entirety of incubation. The plateau and decline phases of AMPA were not reached in all treatments and then the kinetic parameters for AMPA could not be reliably determined. The kinetic parameters of glyphosate decay were thus calculated by fitting with the SFO model (Table 2). The results showed that among all treatments, the decay rate (k), DT_{50} and DT_{90} were similar, with an average of 0.021 day^{-1}, 32.8 days and 108.8 days, respectively, and 8% coefficient of variation.

3.2. Soil microbial respiration and enzyme activity assays

3.2.1. Soil microbial respiration

During the incubation period, significant differences have been observed at the soil basal respiration and substrate-induced respiration of each treatment (Table 3). Soil basal respiration significantly decreased at the first day and then increased and varied from D3 to D30 (Table 3a). Comparing to control experiment (CK), univariate factor, either glyphosate or microplastics added in treatment G1, G2 and M1, didn't show significant differences in soil basal respiration at the same sampling day except in treatment M2. However, soil basal respiration presented the significant differences in the combination treatments, especially in the treatment M2G1 and M2G2. On the same sampling day, soil basal respiration significantly differed under different treatments with high microplastic content, especially those under M2, M2G1 and M2G2.

Substrate-induced respiration significantly higher than soil basal respiration in each correspondence treatments, ranging from 1.60 to 33.61 ppm CO_2 g^{-1} soil h^{-1} (Table 3b). The slight declining of substrate-induced respiration was also detected after 1 day glyphosate applied. Afterwards, it increased significantly and the peak was observed at D3 in all treatment except CK and M2G2 which had a short lag on D7. After 30 days incubation, soil substrate-induced respiration declined significantly, especially in the treatment G1 and G2. Meanwhile, compared with CK treatment, soil substrate-induced respiration presented the similar properties in treatment G1/G2/M1/M1G1/M1G2 while significant higher level of soil substrated-induced respiration rates were observed in treatment M2/M2G1/M2G2 on the same sampling day. However, significant differences of soil substrate-induced respiration has been tested in the treatment M2G2 comparing with other treatments on the same sampling day.

3.2.2. Soil enzyme activity assays

The dynamics of soil β-glucosidase, urease and phosphatase activities were observed throughout the entirety of the incubation period of all treatments (Table 4a–c). β-glucosidase contents ranged from 0.41 μmol g^{-1} h^{-1} to 0.77 μmol g^{-1} h^{-1} and increased slightly after D0 in all treatments (Table 4a). However, β-glucosidase content in CK treatment changed slightly without any significant difference throughout incubation days. Although significant differences of β-glucosidase contents were observed in different treatments at the same sampling day, the changes did not follow the same variation trend at different sampling days. The highest β-glucosidase content was detected in M2 treatment on all sampling days except for M2G1 and M2G2 on D1. β-glucosidase content did not exhibit consistent and significant differences in different treatments with different levels of microplastic addition. Urease contents significantly varied and ranged from 0.46 μmol g^{-1} h^{-1} to 3.71 μmol g^{-1} h^{-1} (Table 4b). Urease content significantly decreased after 30 days incubation in all treatments, approximately 43%–80% comparing with that in D0. The highest urease contents were observed under M2G1 and M2G2 on D0. After 30 days of incubation, urease contents under G1 and G2 treatments were significantly different from those treatments with microplastic addition, especially in those treatments that combine glyphosate

Table 1b
Detection rate of AMPA in soil of different treatments during the incubation period.

Treatment	Detection rate of AMPA* in different sampling day					
	D0	D1	D3	D7	D14	D30
G1	0.05 ± 0.006 d	0.06 ± 0.004 d	0.11 ± 0.001 c	0.13 ± 0.023 c	0.24 ± 0.026 b	0.30 ± 0.010 a
M1G1	0.04 ± 0.006 e	0.05 ± 0.001 e	0.09 ± 0.004 d	0.16 ± 0.013 c	0.24 ± 0.006 b	0.28 ± 0.010 a
M2G1	0.04 ± 0.004 e	0.05 ± 0.002 e	0.09 ± 0.009 d	0.15 ± 0.011 c	0.25 ± 0.004 b	0.28 ± 0.004 a
G2	0.05 ± 0.001 e	0.07 ± 0.002 de	0.08 ± 0.007 d	0.14 ± 0.006 c	0.21 ± 0.020 b	0.29 ± 0.017 a
M1G2	0.05 ± 0.003 e	0.05 ± 0.002 e	0.09 ± 0.005 d	0.15 ± 0.006 c	0.20 ± 0.012 b	0.31 ± 0.018 a
M2G2	0.06 ± 0.004 e	0.07 ± 0.001 e	0.09 ± 0.004 d	0.15 ± 0.008 c	0.21 ± 0.007 b	0.31 ± 0.024 a

*AMPA was transferred as parent glyphosate according to molecular mass. Different lowercase letters within the same row mean significant differences on detection rate of AMPA during the incubation days in the same treatment ($p < 0.05$).

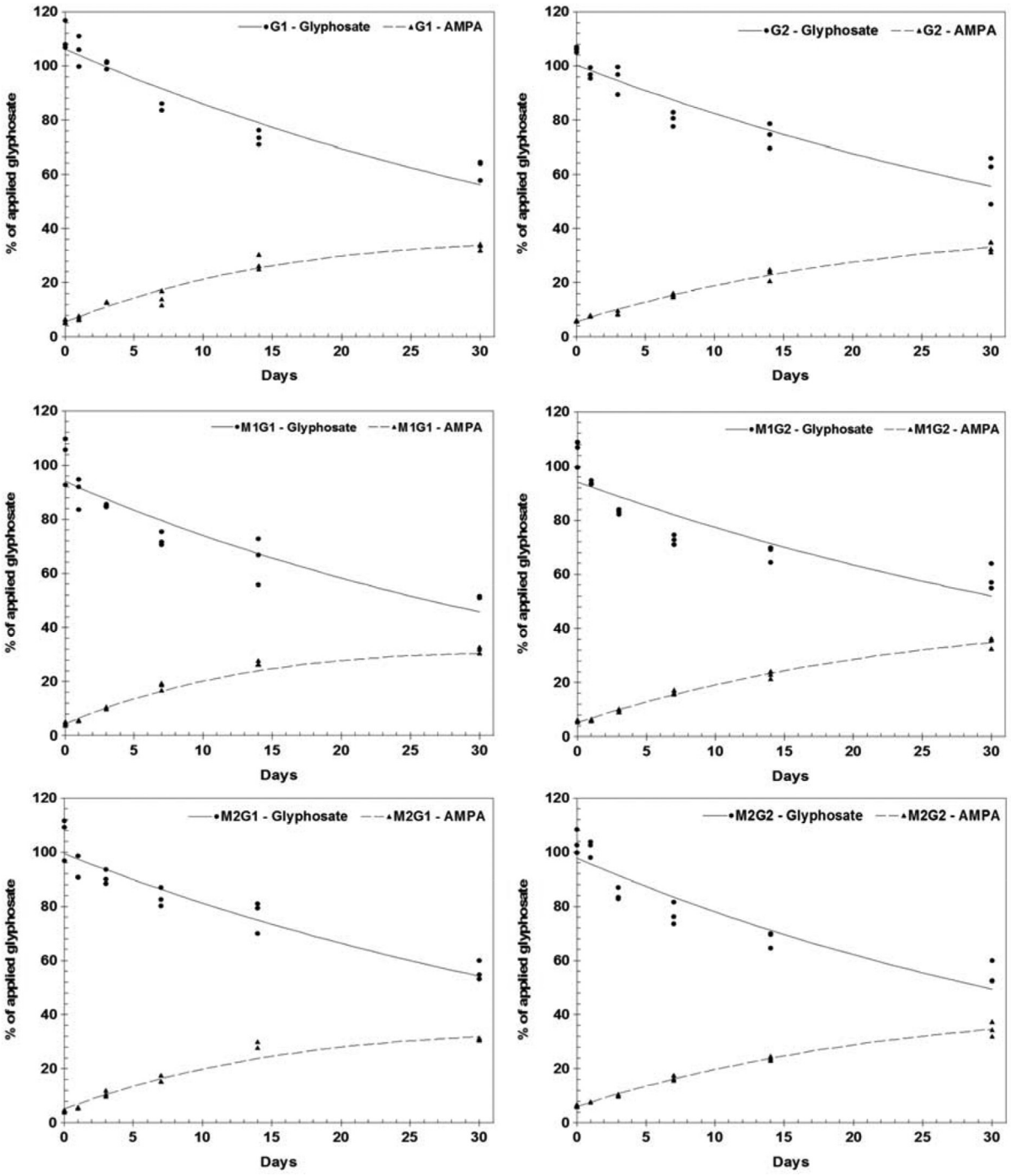

Fig. 1. The kinetics of glyphosate decay and AMPA formation based on the SFO model in the different treatments.

Table 2
Glyphosate decay kinetics parameters in soil for the different treatments applied based on single first-order (SFO) model.

Treatment	C_0±SD (% applied)	$k \pm$ SD (d^{-1})	DT50 (d)	DT90 (d)	χ^2 error (%)
G1	106.1 ± 1.6	0.021 ± 0.002*	32.7	108.5	4.3
M1G1	94.0 ± 1.9	0.024 ± 0.002*	28.9	95.9	5.4
M2G1	99.3 ± 1.6	0.020 ± 0.002*	34.3	113.8	3.5
G2	100.2 ± 1.5	0.020 ± 0.002*	35.2	117.0	3.8
M1G2	94.2 ± 2.0	0.020 ± 0.002*	35.0	116.3	7.0
M2G2	97.8 ± 1.7	0.023 ± 0.002*	30.5	101.2	5.6

* Estimated parameter is significantly different from zero (*t*-test; $p < 0.05$).

Table 3a
Effects of treatments on soil basal respiration during the 30 incubation days.

Treatments	Soil basal respiration rate (ppm-CO_2 g^{-1} h^{-1})					
	D0	D1	D3	D7	D14	D30
CK	3.04 ± 0.95 aBC	0.88 ± 0.23 cE	2.00 ± 0.20 bF	1.93 ± 0.16 bF	2.78 ± 0.13 aD	2.07 ± 0.14 bE
G1	2.72 ± 0.05 abBC	1.15 ± 0.03 cDE	3.07 ± 0.22 aDE	2.55 ± 0.22 abEF	2.92 ± 0.15 abD	2.47 ± 1.48 bcE
G2	3.67 ± 0.42 aB	1.35 ± 0.14 cDE	3.12 ± 0.44 bDE	2.65 ± 0.13 bE	3.12 ± 0.09 bCD	2.94 ± 0.60 bDE
M1	2.68 ± 0.04 aBC	1.02 ± 0.11 bE	2.92 ± 0.16 aE	2.47 ± 0.09 aEF	2.76 ± 0.11 aD	3.28 ± 0.73 aDE
M2	7.15 ± 1.11 abA	3.82 ± 0.86 dA	6.34 ± 0.12 bcA	4.14 ± 0.33 dC	5.42 ± 0.96 cdB	8.17 ± 1.44 aB
M1G1	2.02 ± 0.22 bC	2.04 ± 0.60 bBC	3.40 ± 0.22 aD	3.87 ± 0.59 aCD	3.49 ± 0.35 aC	4.05 ± 0.19 CDa
M1G2	3.35 ± 0.25 bcBC	1.83 ± 0.16 dCD	3.19 ± 0.05 cDE	3.44 ± 0.34 bcD	3.73 ± 0.14 bC	5.63 ± 0.50 aC
M2G1	5.16 ± 0.88 cdB	2.69 ± 0.07 dB	4.61 ± 0.37 cC	5.09 ± 0.04 bcB	6.02 ± 0.33 bB	7.85 ± 0.76 aB
M2G2	6.74 ± 1.10 bA	4.44 ± 0.45 cA	5.12 ± 0.38 cB	7.85 ± 0.87 bA	7.20 ± 0.53 bA	11.48 ± 1.14 aA

Different lowercase letters within the same row mean significant differences in each individual treatment during the incubation days; different capital letters within the same column mean significant differences among treatments in each incubation day ($p < 0.05$).

Table 3b
Effects of treatments on soil substrate-induced respiration during the 30 incubation days.

Treatments	Soil substrate-induced respiration rate (ppm-CO_2 g^{-1} h^{-1})					
	D0	D1	D3	D7	D14	D30
CK	4.83 ± 0.10 aD	6.50 ± 0.69 aC	6.60 ± 2.04 aD	6.67 ± 0.60 aD	6.50 ± 0.53 aF	5.72 ± 1.59 aBC
G1	9.43 ± 0.50 cCD	7.07 ± 0.31 dC	15.27 ± 1.39 aC	8.87 ± 0.95 cCD	11.57 ± 0.96 bDE	1.60 ± 0.96 eD
G2	10.08 ± 0.78 bC	8.67 ± 0.49 cBC	15.57 ± 0.15 aC	9.93 ± 1.19 bC	12.07 ± 0.91 bDE	2.82 ± 0.64 dCD
M1	9.32 ± 1.60b cCD	6.99 ± 0.78 cdC	14.37 ± 2.86 aC	9.00 ± 1.44 bcCD	11.04 ± 0.63 bE	5.13 ± 0.43 dBC
M2	20.95 ± 0.29 bB	17.78 ± 1.96 bA	33.61 ± 4.52 aA	17.64 ± 1.57 bB	17.45 ± 1.24 bB	9.35 ± 1.16 cA
M1G1	10.90 ± 1.27 bcC	10.00 ± 3.57 dBC	15.63 ± 0.45 aC	10.04 ± 0.45 cdC	13.26 ± 0.66 abCD	5.41 ± 0.38 eB
M1G2	11.29 ± 1.16 cC	10.07 ± 0.35 cBC	16.92 ± 1.55 aC	10.57 ± 1.15 cC	14.73 ± 0.43 bC	6.45 ± 0.35 dB
M2G1	14.40 ± 1.96 cdBC	12.69 ± 1.31 deB	22.64 ± 1.00 aB	16.30 ± 1.21 bcB	18.52 ± 1.21 bB	9.91 ± 0.84 eA
M2G2	24.81 ± 5.50 abA	23.70 ± 2.02 bA	28.66 ± 6.40 abA	31.02 ± 2.99 aA	29.49 ± 2.16 abA	10.83 ± 3.03 cA

Different lowercase letters within the same row mean significant differences in each individual treatment during the incubation days; different capital letters within the same column mean significant differences among treatments in each incubation day ($p < 0.05$).

Table 4a
Effects of treatments on soil β-glucosidase during the 30 incubation days.

Treatment	β-glucosidase content (μmol g^{-1} h^{-1})					
	D0	D1	D3	D7	D14	D30
CK	0.48 ± 0.06 bA	0.57 ± 0.02 aC	0.56 ± 0.04 aC	0.52 ± 0.04 aBC	0.56 ± 0.01 aC	0.58 ± 0.02 aC
G1	0.41 ± 0.08 bA	0.57 ± 0.02 aC	0.57 ± 0.01 aC	0.52 ± 0.08 bBC	0.57 ± 0.01 aC	0.59 ± 0.03 aC
G2	0.47 ± 0.02 cA	0.53 ± 0.07 bcC	0.57 ± 0.01 abC	0.48 ± 0.01 cBC	0.57 ± 0.01 abC	0.61 ± 0.02 aC
M1	0.43 ± 0.13 bA	0.61 ± 0.05 aBC	0.62 ± 0.02 aC	0.51 ± 0.03 abBC	0.61 ± 0.02 aBC	0.61 ± 0.03 aC
M2	0.50 ± 0.05 bA	0.66 ± 0.05 aAB	0.73 ± 0.02 aA	0.63 ± 0.10 aA	0.71 ± 0.05 aA	0.71 ± 0.08 aAB
M1G1	0.49 ± 0.02 bA	0.65 ± 0.04 aAB	0.61 ± 0.02 aC	0.53 ± 0.03 bBC	0.60 ± 0.02 aBC	0.62 ± 0.04 aBC
M1G2	0.48 ± 0.02 cA	0.62 ± 0.01 abAB	0.62 ± 0.02 abC	0.50 ± 0.03 bcBC	0.61 ± 0.02 abcBC	0.65 ± 0.01 aBC
M2G1	0.47 ± 0.06 cA	0.77 ± 0.22 aA	0.71 ± 0.06 abAB	0.56 ± 0.08 bcB	0.66 ± 0.02 abcAB	0.77 ± 0.06 aA
M2G2	0.48 ± 0.07 bcA	0.73 ± 0.06 aA	0.64 ± 0.13 abBC	0.45 ± 0.05 cC	0.65 ± 0.13 aAB	0.61 ± 0.08 abC

Different lowercase letters within the same row mean significant differences in each individual treatment during the incubation days; different capital letters within the same column mean significant differences among treatments in each incubation day ($p < 0.05$).

Table 4b
Effects of treatments on soil urease during the 30 incubation days.

Treatments	Urease content (μmol g^{-1} h^{-1})					
	D0	D1	D3	D7	D14	D30
CK	1.83 ± 0.64 aBC	1.82 ± 0.30 aB	1.50 ± 0.36 aAB	1.60 ± 0.06 aAB	1.82 ± 0.44 aAB	1.04 ± 0.27 bDE
G1	2.34 ± 0.57 aBC	1.24 ± 0.02 bC	1.55 ± 0.07 bAB	1.45 ± 0.22 bBC	1.12 ± 0.07 bD	0.46 ± 0.08 cF
G2	2.52 ± 0.66 aB	1.61 ± 0.53 bB	1.20 ± 0.36 bBC	1.16 ± 0.21 bC	1.14 ± 0.22 bD	0.92 ± 0.20 bEF
M1	1.59 ± 0.33 abC	1.87 ± 0.30 aB	1.68 ± 0.36 abA	1.24 ± 0.23 bBC	1.71 ± 0.38 abBC	1.28 ± 0.15 bCD
M2	2.33 ± 0.49 aBC	1.91 ± 0.67 abB	1.21 ± 0.38 bBC	1.63 ± 0.14 abAB	2.38 ± 0.53 aA	1.16 ± 0.24 bCD
M1G1	2.09 ± 0.58 aBC	1.97 ± 0.57 abAB	1.19 ± 0.54 bBC	1.40 ± 0.19 abBC	1.48 ± 0.45 abCD	1.44 ± 0.36 abBC
M1G2	2.47 ± 0.22 bB	2.67 ± 0.35 aA	1.44 ± 0.34 bAB	1.36 ± 0.19 bBC	1.14 ± 0.29 bCD	1.54 ± 0.49 bBC
M2G1	3.37 ± 0.20 aA	1.37 ± 0.50 cC	0.98 ± 0.21 dC	1.67 ± 0.23 bcA	1.36 ± 0.27 cCD	1.84 ± 0.30 bA
M2G2	3.71 ± 0.32 aA	1.50 ± 0.38 bcBC	1.07 ± 0.29 cBC	1.46 ± 0.31 bcBC	1.66 ± 0.14 bBC	1.66 ± 0.16 bB

Different lowercase letters within the same row mean significant differences in each individual treatment during the incubation days; different capital letters within the same column mean significant differences among treatments in each incubation day ($p < 0.05$).

Table 4c
Effects of treatments on soil phosphatase during the 30 incubation days.

Treatments	Phosphatase (μmol g^{-1} h^{-1})					
	D0	D1	D3	D7	D14	D30
CK	1.97 ± 0.18 bD	2.65 ± 0.24 aD	2.27 ± 0.14 aD	2.01 ± 0.15 aD	2.04 ± 0.02 aCD	1.65 ± 0.06 bD
G1	2.17 ± 0.12 bCD	2.62 ± 0.21 aCD	2.44 ± 0.19 aCD	2.17 ± 0.05 bD	2.08 ± 0.09 bBC	1.70 ± 0.08 cD
G2	2.29 ± 0.06 bBC	2.50 ± 0.06 aD	2.58 ± 0.20 bD	2.25 ± 0.11 cCD	1.88 ± 0.02 cDE	1.61 ± 0.02 dD
M1	2.04 ± 0.09 deD	2.95 ± 0.04 aBC	2.51 ± 0.18 bCD	2.25 ± 0.12 cCD	2.11 ± 0.10 cdBC	1.85 ± 0.02 eC
M2	2.49 ± 0.14 cAB	3.39 ± 0.07 aA	3.17 ± 0.23 aB	2.83 ± 0.25 bA	2.56 ± 0.09 bcA	2.37 ± 0.03 cAB
M1G1	2.52 ± 0.09 aAB	2.59 ± 0.18 aD	2.70 ± 0.07 aC	2.18 ± 0.16 bD	1.76 ± 0.04 cE	1.84 ± 0.11 cC
M1G2	2.37 ± 0.19 bBC	2.44 ± 0.01 bD	3.09 ± 0.21 aB	2.45 ± 0.18 bBC	1.84 ± 0.09 cE	1.67 ± 0.03 cD
M2G1	2.66 ± 0.24 cA	3.16 ± 0.16 bAB	3.59 ± 0.16 aA	2.60 ± 0.15 cdAB	2.26 ± 0.23 eB	2.30 ± 0.06 deB
M2G2	2.49 ± 0.08 cAB	3.25 ± 0.08 bAB	3.58 ± 0.13 aA	2.46 ± 0.04 cBC	2.18 ± 0.13 dBC	2.48 ± 0.12 cA

Different lowercase letters within the same row mean significant differences in each individual treatment during the incubation days; different capital letters within the same column mean significant differences among treatments in each incubation day ($p < 0.05$).

and microplastics. The differences of urease contents among treatments varied slightly at the same sampling days. No consistent differences in urease contents, however, were observed under treatments with different levels of glyphosate application. In addition, comparing to CK treatment, phosphatase contents significantly increased at D0, peaked at D3 (Table 4c), declined and varied slightly until D30 in all treatments. Compared soil enzyme activities on the same incubation day in different treatments, phosphatase content varied in different glyphosate and microplastic additions. Phosphatase contents under treatment with high levels of microplastic additions (M2, M2G1 and M2G2) were significantly different on each observation day.

3.3. Microplastic residues

Particle sizes of microplastics on D0 and D30 in different treatments were compared (Table 4). Initially, 58% and 36% of microplastic particles clustered at 125–250 μm and 100–125 μm respectively. Particle size distribution changed significantly although the sizes of the majority of microplastic particles remained at 125–250 μm and 100–125 μm. In all treatments, the number of microplastic particles with sizes of 125–250 μm decreased by approximately 20% and those with sizes of 100–125 μm dominated after 30 days of incubation. The number of microplastic particles in different size groups increased differently. Comparing with initial particle sizes of microplastics, the percentage of smaller particles increased significantly in treatment M1, M1G1 and M1G2, especially particles with sizes of 100–125 μm. Particles sizes under M2, M2G1 and M2G2 showed lower transformation rates from larger to smaller particle sizes. Significant differences of particle size clustered less than 50 μm were observed in treatment M1, M1G1 and M1G2, approximately 10 times higher than that original particle size. In addition, based on the mass balance, the recovery rates for the microplastics ranged from 108% to 94% in treatments after 30 days incubation.

4. Discussion

Plastic debris poses threats to wildlife, absorbs toxic chemicals and degrades into smaller particles, such as microplastics (Barnes et al., 2009; Law, 2017; Lönnstedt and Eklöv, 2016). Although numerous studies have been focused on the movement, distribution and effects of plastic debris in aquatic systems (Galloway and Lewis, 2016; Law, 2017; Vandermeersch et al., 2015), only a few studies have investigated these aspects of plastic debris in terrestrial ecosystems and soil (Huerta et al., 2017; Huerta Lwanga et al., 2016; Rillig, 2012; Rillig et al., 2017a). The intensive use of plastic film mulching produces considerable amounts of plastic debris, which contaminates arable land at a rate of approximately 50–260 kg hm^{-2} (Yan et al., 2010). "White pollution," which is akin to pesticide contamination, is an urgent concern in the development of sustainable agriculture (Liu et al., 2014). With long-term weathering and interaction with the soil, macro/micro-plastics may influence the behaviours of existing compounds in the soil matrix (Hüffer and Hofmann, 2016). The results of the present study showed that the addition of microplastics didn't affect the degradation behaviour of glyphosate which followed a SFO kinetic model in all treatments. Glyphosate exhibited an average half-life of 32.8 ± 2.6 days with a very low standard deviation among all treatments, suggesting that microplastic addition does not affect glyphosate degradation. It is explained that glyphosate is a polyprotic acid that can occur as mono- and divalent anions (Sheals et al., 2002) and an organophosphate compound that can bind to the soil with ligand exchange through the phosphonic acid moiety (Al-Rajab et al., 2008). Microplastics, such as the polypropylene powder used in this study, are polymers that are resistant to be decomposed by almost all organic solvents and strong oxidants. As shown by the results of a batch experiment in which microplastics were spiked with glyphosate (unpublished data and not mentioned in this study), glyphosate and microplastics barely interact under the conditions of the present study. The half-life of glyphosate varies significantly in accordance with soil properties, soil moisture and temperature, ranging from days to months (Bento et al., 2016; Litz et al., 2011). Accordingly, the metabolite AMPA continuously increased during the incubation period in all treatments but did not reach a plateau and a decline phase as shown in previous study as mentioned. This behaviour precluded the calculation of its half-life time (Fig. 1). Nevertheless, similar to the findings of Bento et al. (2016), AMPA is more persistent in soil than its parent glyphosate and continuously increased during the whole incubation days (Fig. 1). Although microplastics didn't adsorb glyphosate, its potential risk as a vector for other compounds, such as PAHs, PCBs, HCHs, DDTs, requires research attention (Zhang et al., 2015b; Ziccardi et al., 2016).

Plastic residues in soil decrease soil saturated hydraulic conductivity (Wang et al., 2015) and influence soil microbial communities (Jiang et al., 2014) and soil macrofuna activities (Huerta et al., 2016). Soil microbial communities, in turn, have a crucial role in nutrient cycling and influences pollutant behaviour, including the mineralization, biodegradation and detoxification of toxic compounds (Rose et al., 2016). With the addition of plastic residues, soil microbial carbon, nitrogen, soil fluorescein diacetate hydrolysis and soil dehydrogenase declined by 28.9%–73.5%, 38.2%–76.2%, 1.6%–30.7%, 14.9%–59.0%, respectively (Wang et al., 2016a). However, these results only focused on the responses of soil microbial activities under the addition of larger particle size of plastic debris (20 mm × 20 mm) instead of microplastics. Our study initially presented the effects of microplastics and glyphosate addition on

Table 5
The distribution of microplastics size between initial added particles and those in soil samples of treatments after 30 days incubation.

Treatments	Particle size (%)					Recovery rate (%)
	250-125 μm	125-100 μm	100-63 μm	63-50 μm	<50 μm	
Original size	58.35 ± 8.69 A	35.86 ± 3.57 C	2.27 ± 0.01 B	1.07 ± 0.02 C	0.63 ± 0.02 E	98 ± 4#
M1	37.79 ± 1.31 D	46.72 ± 5.89 A	5.38 ± 2.04 A	3.92 ± 0.95 B	6.20 ± 1.48 B	108 ± 1
M1G1	39.52 ± 2.72 D	43.63 ± 5.03 B	4.45 ± 1.89 A	5.43 ± 0.37 A	6.98 ± 0.57 B	101 ± 2
M1G2	35.46 ± 4.55 E	43.33 ± 1.48 B	6.20 ± 0.69 A	6.31 ± 1.62 A	8.69 ± 1.28 A	101 ± 3
M2	45.61 ± 7.22 C	46.77 ± 4.02 A	2.76 ± 1.56 B	2.91 ± 1.30 B	1.95 ± 0.35 C	103 ± 4
M2G1	45.82 ± 0.68 C	47.30 ± 1.19 A	2.11 ± 0.09 B	2.60 ± 0.12 B	2.17 ± 0.49 C	99 ± 1
M2G2	45.01 ± 3.18 B	49.54 ± 1.62A	2.24 ± 0.69 B	1.49 ± 0.66 C	1.56 ± 0.21 D	98 ± 2

Different capital letters within the same column mean significant differences among treatments ($p < 0.05$).
The recovery for original particles means the quantification of detection method.

soil microbial respiration and enzyme activities. In all treatments, particularly in those treatments with high levels of microplastic addition, soil basal respiration decreased by approximately 40% a day after glyphosate application and gradually increased afterwards (Table 3a). Substrate-induced respiration, however, varied during the incubation period, following declining-peaking-declining trend (Table 3b). It is said that the addition of microplastics affects porosity and air circulation (Zhang et al., 2015a), which are both related to soil microbial respiration. Therefore, in the present study, the addition of microplastics increased microbial respiration rate, particularly substrate-induced respiration comparing to CK treatment. A meta-analysis revealed that glyphosate application significantly influences soil microbial activities and temporarily enhances soil microbial respiration for less than 60 days (Nguyen et al., 2016). Our results showed that basal respiration was slightly enhanced under G1 and G2 treatment after 30 days of incubation but substrate-induced respiration showed the opposite trend. In this study, glyphosate was applied at a rate greater than 10 mg kg^{-1} but less than 100 mg kg^{-1}. Thus, glyphosate application did not significantly alter soil microbial respiration as Nguyen et al. (2016) summarized. Soil β-glucosidase, urease and phosphatase activities are linked to carbon, nitrogen and phosphorous cycling, respectively, and changed during the incubation period. Phosphatase activities differed significantly in different treatments, especially in treatments with higher contents of glyphosate and microplastics (Table 4c). Phosphatase activity is related to the P source in the soil (Busato et al., 2016) and microorganisms in soils with limited P sources might be stimulated by glyphosate application (Liu et al., 2017). Although microplastic addition increased soil phosphatase activity, the mechanism that underlies this response should be elucidated by future studies.

Although plastic is durable and resistant, its decomposition relies on its type and exposure conditions. Nauendorf et al. (2016) showed that polyethylene and biodegradable plastic bags were biodegraded under the exposure of marine sedimentary conditions for 100 days, indicating a long-term plastic sink in deep sediment layers. Fortunately, it has been reported that mealworms can degrade polystyrene (Yang et al., 2015c), and the main gut bacterial strains have been identified, which contribute to the depolymerization and biodegradation of petroleum-based plastics (Yang et al., 2015d). A novel bacterium that can degrade and assimilate plastic has been isolated from natural microbial communities (Huerta et al., 2018; Yoshida et al., 2016). These findings imply that plastic biodegradation or remediation for plastic contamination are viable (Krueger et al., 2015). A previous study showed that earthworms were able to digest microplastics and reduce them into smaller particle sizes after 60 d of incubation (Huerta Lwanga et al., 2016). Interestingly, in this study, we observed that the sizes of the microplastic particles were heterogeneously distributed, with diverse particle sizes and smaller particles formed in the bare soil (Table 5). Our findings and those of other studies on microplastics in terrestrial ecosystems (Huerta et al., 2017; Huerta Lwanga et al., 2016) indicate that further research is required to obtain more information on the responses of natural soil bacterial communities to plastic debris.

In addition, plastic film mulching has been widely used in vegetable and crop production, and it is considered a promising practice in agriculture thanks to its benefits for conserving soil moisture, improving soil temperature, and preventing weeds growth. However, adverse effects arise from cumulative plastic residues (macro/micro-meters), plastic additives and likely adsorbed agrochemicals, which finally may impact soil quality in the long term (Steinmetz et al., 2016). Although the biodegradable plastic film product, such as starch-based plastic film, has been developed, their costs and performance inhibit their widespread use in large-scale farming systems (Fei et al., 2015; Li et al., 2014). Therefore, the impacts of plastic debris and pesticide on soil quality in terrestrial ecosystems, especially in the farmlands of China where plastic film mulching and pesticides are frequently used, should receive more attention.

5. Conclusion

The effects of microplastic addition on glyphosate decay and on soil microbial activities were investigated in this study. Experimental data were obtained over a 30-day incubation period and fitted to a SFO decay kinetics model. Glyphosate exhibited similar half-lives in the different treatments with or without microplastics addition. AMPA persisted longer in soil and did not exhibit plateau and decline phases over the entirety of the incubation period. Soil microbial respiration significantly changed during incubation with the addition of high microplastic content. Soil β-glucosidase, urease and phosphatase concentrations varied with the addition of high microplastic content. In each treatment, the size distribution of microplastics significantly changed. Moreover, particles that were smaller than the initially added microplastics formed over the incubation period indicating the potential risks for leaching or entraining to water system. The present study, thus, provided prime information about the responses of glyphosate behaviour and soil microbial activities to microplastic addition in terrestrial ecosystems. Further study is needed to investigate other agrochemicals' behaviour and the response of soil properties and plant growth in the farmland with plenty of plastic residues (micro/macro-plastics).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.07.006.

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