Received: 9 October 2020 | Revised: 26 October 2021 | Accepted: 18 February 2022

DOI: 10.1002/ldr.4243

RESEARCH ARTICLE

WILEY

Simazine degradation in agroecosystems: Will it be affected by the type and amount of microplastic pollution?

Jie Zhou[1] | Yuan Wen[1] | Hongguang Cheng[2] | Huadong Zang[1] | Davey L. Jones[3,4]

[1]College of Agronomy and Biotechnology, China Agricultural University, Beijing, PR China

[2]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, PR China

[3]School of Natural Sciences, Bangor University, Bangor, Gwynedd, UK

[4]SoilsWest, Centre for Sustainable Farming Systems, Food Futures Institute, Murdoch University, Murdoch, Western Australia, Australia

Correspondence
Huadong Zang, College of Agronomy and Biotechnology, China Agricultural University, Beijing, PR China.
Email: zanghuadong@cau.edu.cn

Funding information
Earmarked Fund for China Agriculture Research System, Grant/Award Number: CARS-07-B-5; China Scholarship Council, Grant/Award Number: 201606850093; UK-China Virtual Joint Centre for Agricultural Nitrogen, Grant/Award Number: BB/N013468/1; UK Global Challenges Research Fund (GCRF) project awarded to Bangor University, Grant/Award Number: NE/V005871/1

Abstract

Plastics and herbicides represent two of the most extensive and persistent anthropogenic contaminants entering agroecosystems. The synergistic interaction of these pollutants on soil health, however, remains poorly understood. For the first time, we investigated the behavior of a common selective triazine herbicide (simazine) in soil containing 0%, 1%, 5%, 10%, and 20% (w/w) of two commonly found microplastics, namely polyethylene (PE) and polyvinyl chloride (PVC). The mineralization of ^{14}C-labeled simazine in soil decreased with the presence of both PE and PVC as indicated by the lower total $^{14}CO_2$ loss. Consequently, the half-life of simazine increased in the presence of microplastics, although there was little difference between microplastic types. The ratio of fungi-to-bacteria in the soil increased by 9%–18% after 1% of microplastics addition, while enzyme activities involved in C-cycling decreased by 20%–46% in soil amended with PVC relative to the control. Further, enzyme activities were negatively correlated with the half-life of simazine when added with PVC. Therefore, we ascribe the repression in simazine degradation to changes in microbial community structure (increased fungi-to-bacteria ratio) and reduced enzyme activities. Overall, microplastics accumulation in soil decreases herbicide breakdown resulting in herbicide residuals remaining, which in turn, may increase their risk of reaching ground or surface waters.

KEYWORDS
agrochemical degradation, enzyme activity, microplastics, simazine residuals, soil quality

1 | INTRODUCTION

Petroleum-based plastics (i.e., plastic mulch) are widely used in agroecosystems, with global production of agroplastics now exceeding six million tonnes per year (Vox et al., 2016). The extensive use of plastics on land has resulted in the supposition that the accumulation of microplastics in soil might be much larger compared with the ocean (Horton et al., 2017). Due to their synthetic nature, microorganisms find it difficult to assimilate and mineralize plastic polymers, leading to their progressive accumulation in soil when used over repeated cropping cycles (Ng et al., 2018). Although there have been several studies on the impact of microplastics in marine systems, the potential effects of microplastics in agroecosystems remain largely unexplored (Rillig et al., 2019; Yang et al., 2018; Zang et al., 2020; Zhou, Gui, et al., 2021). Therefore, investigating the potential environmental effects of microplastic pollution in agroecosystems and specifically, their impact on plant-soil health is urgently required.

Simazine (2-chloro-4,6-bis-ethylamino-*s*-trizaine) is one of the most widely used herbicides for weed control in agriculture (Seeger et al., 2010). When applied to fruit and vegetable crops, ca. 30% of these pesticides inevitably falls onto the soil surface (Agnihotri et al., 1994; Barber & Parkin, 2003). Previous studies have shown that simazine can be long-lasting in soil, persisting from weeks to months depending on the soil type and prevailing climate (Jones et al., 2011;

PPDB, 2015; Yang et al., 2018). This makes simazine susceptible to leaching or surface water runoff (Jiang et al., 2011; Silva et al., 2019). This is supported by studies in the USA and Europe where simazine is the second most constantly reported herbicide in surface water and groundwater (Silva et al., 2019; Toccalino et al., 2014), and is commonly detected as a contaminant of freshwater in China (Cheng et al., 2017; Li et al., 2018). Therefore, understanding the rate of herbicide transformation in agroecosystems is an important component when evaluating their fate and persistence in the environment (Seeger et al., 2010; Silva et al., 2019).

Degradation of herbicides involves both biotic transformation processes-mediated by microorganism or plants and abiotic processes such as chemical and photochemical reactions (Arias-Estévez et al., 2008; Bento et al., 2016; Fenner et al., 2013). As microplastics can influence the soil's physicochemical properties (de Souza Machado et al., 2018; Zhou, Wen, et al., 2021), it is expected that microplastics may have multiple effects on soil microbial activity and functioning (Zang et al., 2020; Zhou, Gui, et al., 2021), thereby influencing herbicide degradation and persistence in agroecosystems (Steinmetz et al., 2016; Yang et al., 2018). Moreover, many herbicides are known to easily sorb to microplastics such as polyethylene (PE) which are widely used in agriculture (Gong et al., 2019; Hüffer et al., 2019), which could reduce their bioavailability and further influence herbicide degradation and movement. Further, the impact of microplastics in agroecosystems on herbicide movement and degradation is likely to be of significance based on studies with macroplastics (Ramos et al., 2015; Yang et al., 2018).

Here, we aim to evaluate the effect of different doses of PE and polyvinyl chloride (PVC) (1%, 5%, 10%, 20%, w/w) on simazine degradation and thus its residence time in soil. We selected these plastic types as they represent the most commonly used plastics throughout the world, accounting for 29.6% and 10.4% of world plastic waste (Kasirajan & Ngouajio, 2012). We hypothesized that microplastics addition would change the soil microbial community and thus alter its functioning; as a consequence we predict that this will decrease the rate of herbicide degradation and subsequently increase its residence time in soil. Second, we hypothesized that this enhanced herbicide persistence would occur regardless of microplastic type.

2 | MATERIALS AND METHODS

2.1 | Experiment set-up and soil sampling

Soil was sampled from the Ap-horizon (0–20 cm) of a grassland in Abergwyngregyn, Gwynedd, North Wales (53°14′N, 4°01′W). The average annual precipitation is 1050 mm with an average annual temperature of 10.8°C, with a range of −10°C to 28°C. The site has a sandy clay loam textured Eutric Cambisol soil type (FAO, 2014). The soil has no previous history of plastic or simazine use. After air-drying, the soil was sieved to pass 5 mm, and then mixed. Visible roots and plant litter were removed prior to incubation. The soil had a pH (H_2O) of 5.7, organic C content of 3.5%, and total *N* of 0.26%. Detailed information on the soil is presented in Zang et al. (2020).

Pots (11 × 8 × 17 cm) were filled with 500 g of air-dried soil and placed in a climate -controlled room. PE and PVC microplastics (<125 μm diameter; Sigma-Aldrich) were added at rates of 1%, 5%, 10%, and 20% of soil (w/w). The control treatment contained soil (500 g) without microplastics, but with comparable soil physical disturbance (Zhou, Gui, et al., 2021). Each treatment consisted of four replicates, yielding a total of 36 pots. Every 3 days, plants were watered to maintain the soil moisture at a gravimetric moisture content of about 25% (60% of water holding capacity, equal to field moist conditions) throughout the experiment by weighing the pots and replacing any water lost. Four wheat seeds (*Triticum aestivum* L.) were planted in each pot after 2 weeks (Zang et al., 2020). The levels of microplastic contamination were used to reflect the localized disposal of plastics in agroecosystems (e.g., residues are plowed into the soil at end of the growing season leading to localized hotspots of plastic pollution) and was based on field investigations (up to 6.7%) and a literature review (up to 20%) (Fuller & Gautam, 2016; Qi et al., 2020; Zhou, Wen, et al., 2021). We amended very large amounts of microplastic to simulate soil hotspots with higher contamination levels (1%–20%) (Zhou, Gui, et al., 2021).

After 35 days of growth, the plants were harvested and the pots were destructively sampled. The whole soil was passed through a 2-mm sieve to remove visible roots and plant litter and then homogenized. Subsequently, the soil samples were divided into sub-samples. One sub-sample from each pot was stored at −80°C for phospholipid fatty acid (PLFA) profiling of the microbial community, while another was stored at 4°C to measure enzyme activities and simazine mineralization (within 3 days of collection).

2.2 | PLFA analysis

PLFA was analyzed based on the method described by Bartelt-Ryser et al. (2005). Briefly, 20 g of fresh soil from each pot was extracted with a one-phase mixture of chloroform, methanol, and aqueous citric acid (1:2:0:8, *v/v/v*, pH 4.0), chloroform and citric acid to achieve a separation of two liquid phases. PLFAs were separated from neutral lipids and glycolipids by solid phase extraction and analyzed by gas chromatography (GC) (Hewlett Packard 5890 GC coupled to a mass selective detector 5971A). In total, 70 fatty acids were detected and quantified. Of these, fatty acids representing >0.5% of the total PLFA were used for biomarker and taxonomic group annotation. Detailed bacterial and fungal PLFAs groupings are given in Zang et al. (2020).

2.3 | Soil exoenzyme activity

The activity of four hydrolytic enzymes involved in C (β-1,4-glucosidase, xylosidase, cellobiohydrolase) and N (chitinase) cycling were determined following the protocol of Wen, Zang, Ma,

et al. (2019) and Zhou et al. (2020). In brief, 1 g of fresh soil was suspended in 50 ml sterile water and shaken for 30 min. After low-energy sonication (2 min, 40 J s^{-1}) by ultrasonic disaggregation, soil suspension (50 μl), MES buffer (50 μl) and the corresponding enzyme substrate (100 μl) at concentrations of 400 μmol g^{-1} were added to 96-well black microplates. Fluorescence values were read at 0, 30, 60, and 120 min using a microplate fluorometer (Victor^3 1420-050 Multi label Counter; PerkinElmer) with excitation and emission filters at 355 and 460 nm, respectively (Zhou et al., 2020).

2.4 | Simazine mineralization

Simazine mineralization was measured as described by Boddy et al. (2008) and Wen, Zang, Freeman, et al. (2019). In brief, fresh soil (dry weight equivalent of 0.5 g) was added to a sterile 50 ml centrifuge tube, placed at room temperature (20°C) and equilibrated for 3 days at a 20% gravimetric moisture content before simazine addition (Jones et al., 2011). Then, 100 μl of ^{14}C-ring-uniformly labeled simazine (6-chloro-N,N′-diethyl-1,3,5-triazine-2,4-diamine; 5 mCi $mmol^{-1}$; Sigma Chemical Co.) solution (0.5 μg simazine dissolved in 100 μl distilled water) was added to the soil surface. The amount of simazine addition was based on the normal application of ~1.5 kg ha^{-1} and the assumption that ~30% would fall onto the soil surface (Barber & Parkin, 2003; Cheng et al., 2017). Subsequently, a vial containing 1 M NaOH (1 ml) was placed inside each tube to trap evolved CO2 and the container sealed. At 1, 3, 5, 8, 17, 25, 32, 45, and 57 hr after simazine addition, the NaOH solutions was changed to measure ^{14}CO2 emissions. The timing for CO_2 trap replacement was chosen because 82%–96% of available C substrates are typically mineralized within 72 h (Jones et al., 2018; Wen, Zang, Freeman, et al., 2019). Optiphase-3 alkali compatible scintillation cocktail (Wallac EG&G Ltd.) was added to the NaOH in the $^{14}CO_2$ traps and the amount of ^{14}C present determined by liquid scintillation counting with automated quench correction (Wallac 1409 scintillation counter; Wallac EG&G Ltd.).

2.5 | Calculations

To calculate the simazine mineralization rate, a two-pool exponential decay model was fitted to the evolved $^{14}CO_2$ (Wen, Zang, Freeman, et al., 2019). ^{14}C-simazine can be divided into two pools in soil: (1) the fast-degrading C pool, represents the substrate-C that is rapidly assimilated by microorganisms as an energy or nutrient source, leading to a rapid efflux of $^{14}CO_2$; (2) the slow-degrading C pool which constitutes the non-extractable residues (Krutz et al., 2009; Laabs et al., 2002). Therefore, a double first order decay model (two-step process) can be used to explain simazine mineralization as follows (Glanville et al., 2016; Wen, Zang, Freeman, et al., 2019; Zang et al., 2020):

$$S = a_1 \times e^{-k_1 t} + a_2 \times e^{-k_2 t} \quad (1)$$

Where: S indicates the amount of ^{14}C remaining in the soil, *t* is the time after ^{14}C-simazine addition (h). a_1 describes the pool size for the fast mineralization phase and k_1 is the rate constant for a_1. The proportion of added ^{14}C allocated to the slow mineralization pool is defined as a_2, while k_2 is the rate constant for a_2 (Wen, Zang, Freeman, et al., 2019).

The half-life of the simazine ($S_{1/2}$) was determined as follows (Wen, Zang, Freeman, et al., 2019; Zang et al., 2020):

$$S_{1/2} = \frac{a_1 + a_2}{2} \quad (2)$$

2.6 | Statistical analyses

All data were expressed as means ($n = 4$) ± standard errors (SE). A one-way ANOVA analysis with Fisher's least significant difference was used to examine the influence of microplastic type and dose on $^{14}CO_2$ evolution, simazine half-life, enzyme activity, and the ratio of fungi to bacteria. The Shapiro–Wilk and Levene-test were used to test the normality and homogeneity of variance for each variable based on the entire set of residuals from the whole model (i.e., $4 \times 5 = 20$). Any data that were not normally distributed were $\log_{10}$ transformed (fungi-to-bacteria ratio, ^{14}C-simazine remaining in the soil). Residuals were checked for a normal distribution using the Shapiro–Wilk test. All differences were considered significant at $p \leq 0.05$. The significant effects of microplastic types and doses on the half-life of simazine, C-degrading enzymes, N-degrading enzymes, and Fungi/Bacteria were determined by variation partitioning analysis using the vegan package in R 3.4.0.

3 | RESULTS

3.1 | Influence of microplastics on simazine mineralization

Regardless of PVC dose, the total amount of simazine remaining in the soils increased by 0.32%–1.76% compared with the unamended control treatment after 57 hr ($p < 0.05$, Figure 1). The amount of simazine remaining in soil added with the higher dose of PE (i.e., 5%–20%) was 1.14%–1.27% higher than that in the plastic-free control soil ($p < 0.05$, Figure 1b), whereas it did not show a significant difference to the 5% to 20% PE addition treatments ($p > 0.05$, Figure 1). Furthermore, 1% PVC addition increased the half-life of simazine mineralization by almost 1 day compared with the control soil ($p < 0.05$, Figure 2a), while no significant difference was seen for the 1% to 20% PVC treatments ($p > 0.05$). There was no significant difference in the simazine mineralization rate between the unamended control soil and 1% addition of PE ($p > 0.05$). However, the half-life of simazine increased by 0.5 day in soil with 5% of PE addition relative to soil with 1% of PE ($p < 0.05$), then it remained stable until 20% ($p > 0.05$, Figure 2b). At an addition rate of 1% PVC, the half-life of simazine was 0.5 day longer compared with soils containing PE ($p < 0.05$, Figure 2). When the dose of microplastics

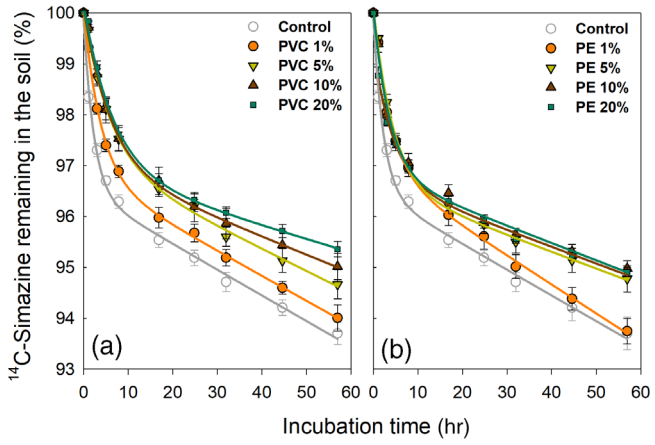

FIGURE 1 ^{14}C-simazine remaining in the soil amended with different types and amounts of microplastics. The microplastics used here were polyvinyl chloride and polyethylene at soil addition rates of 1%, 5%, 10%, and 20% by soil dry weight. Data are means ± standard errors ($n = 4$) [Colour figure can be viewed at wileyonlinelibrary.com]

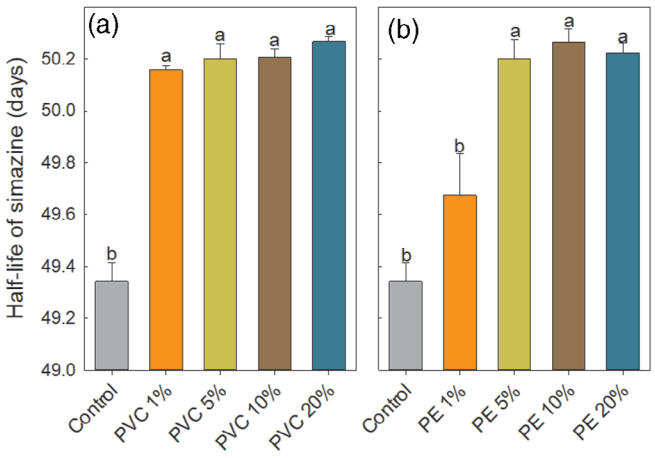

FIGURE 2 The half-life of simazine in the soil amended with different types and amounts of microplastics. The microplastics used here were polyvinyl chloride and polyethylene at soil addition rates of 1%, 5%, 10%, and 20% by soil dry weight. Data are means ± standard errors ($n = 4$). Letters indicating a significant difference between dose of each microplastics and control ($p < 0.05$). Note the *x*-axis is not crossing the *y*-axis at value zero [Colour figure can be viewed at wileyonlinelibrary.com]

rose to 5%–20%, however, the half-life of simazine was not significantly different between PVC and PE addition ($p > 0.05$).

3.2 | Influence of microplastics on soil microbial community and enzyme activity

Compared with the plastic-free control soil, the ratio of fungi-to-bacteria was 9% and 18% higher in the soil with 1% of PVC and PE, respectively ($p < 0.05$, Figure 3). The C-degrading enzyme activity (the sum of β-glucosidase, xylosidase, and cellobiohydrolase) was 20%–

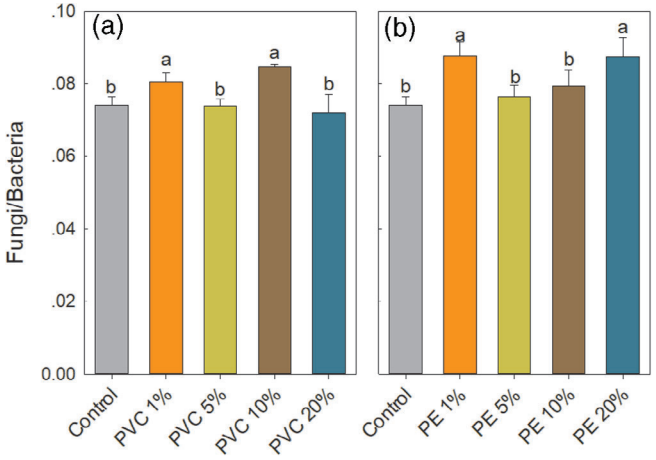

FIGURE 3 The fungi and bacteria ratio (based on phospholipid fatty acid analysis) in soil amended with different types and amounts of microplastics. The microplastics used here were polyvinyl chloride and polyethylene at soil addition rates of 1%, 5%, 10%, and 20% by soil dry weight. Here, the 18:2w6c was indicated as fungi, and the sum of 14:0 iso, 15:0 iso, 15:0 anteiso, 15:1 iso w6c, 15:1 iso w9c, 16:0 iso, 17:0 iso, 17:0 anteiso, 17:1 iso w9c, and 16:1w7c, 16:1w9c, 17:1w8c, 17:0 cyclo w7c, 18:1w5c, 18:1w9c, 18:1w7c, 19:0 cyclo w7c, as well as 16:0 10 methyl, 17:0 10 methyl, 17:1w7c 10 methyl, 18:0 10 methyl, 18:1w7c 10 methyl were viewed as bacteria. Data are means ± standard errors ($n = 4$). Letters indicating a significant difference between dose of each microplastics and control ($p < 0.05$) [Colour figure can be viewed at wileyonlinelibrary.com]

25% lower in soil added with PVC from 1% to 10%, while it decreased by 46% in soil added with 20% of PVC, compared with the control soil ($p < 0.05$, Figure 4a). However, the C-degrading enzymes decreased by 22% in the soil amended with 1% PE ($p < 0.05$, Figure 4b), whereas it did not show a significant difference in the 5% to 20% of PE addition treatments ($p > 0.05$). PVC addition did not affect N-degrading (chitinase) enzyme activity, whereas the N-degrading enzymes decreased in the 1% and 20% PE addition treatments relative to the control soil ($p < 0.05$, Figure 4d).

Microplastic dose played the strongest role and contributed to 80.4%, 28.3%, 37.1%, and 29.5% to the variability of the half-life of simazine, C-degrading enzymes, N-degrading enzymes, and fungi-to-bacteria ratio, respectively (Figure 5). The C-degrading enzymes and fungi-to-bacteria ratio were also strongly affected by microplastic type (Figure 5).

In soil amended with PVC, we found that C-degrading enzymes were positively correlated with gram positive bacteria ($p < 0.05$, Figure 6a). Further, the half-life of simazine was negatively correlated with C-degrading enzymes ($p < 0.05$). However, there was no significant relationship between C- and N-degrading enzymes and half-life of simazine in soil amended with PE ($p > 0.05$, Figure 6b).

4 | DISCUSSION

Consistent with our first hypothesis, contamination of soil with microplastics decreased the rate of simazine decomposition as evidenced

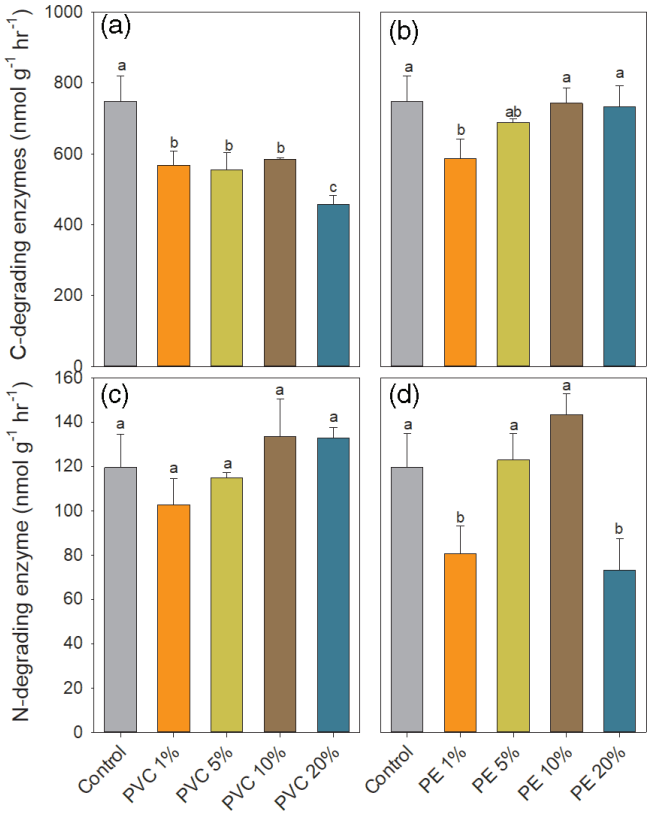

FIGURE 4 The C-degrading enzyme activities (the sum of β-glucosidase, xylosidase, and cellobiohydrolase) and N-degrading enzyme (chitinase) activity in soil amended with different types and amounts of microplastics. The microplastics used here were polyvinyl chloride and polyethylene at soil addition rates of 1%, 5%, 10%, and 20% by soil dry weight. Data are means ± standard errors ($n = 4$). Letters indicating a significant difference between dose of each microplastics and control ($p < 0.05$) [Colour figure can be viewed at wileyonlinelibrary.com]

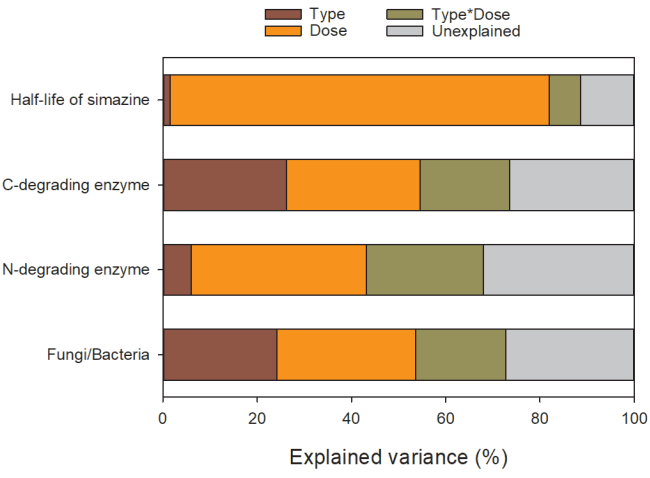

FIGURE 5 Contribution of the two microplastic factors (type and dose) and their interactions on the variation of simazine half-life, C-degrading enzymes, N-degrading enzymes, and the ratio of fungi and bacteria [Colour figure can be viewed at wileyonlinelibrary.com]

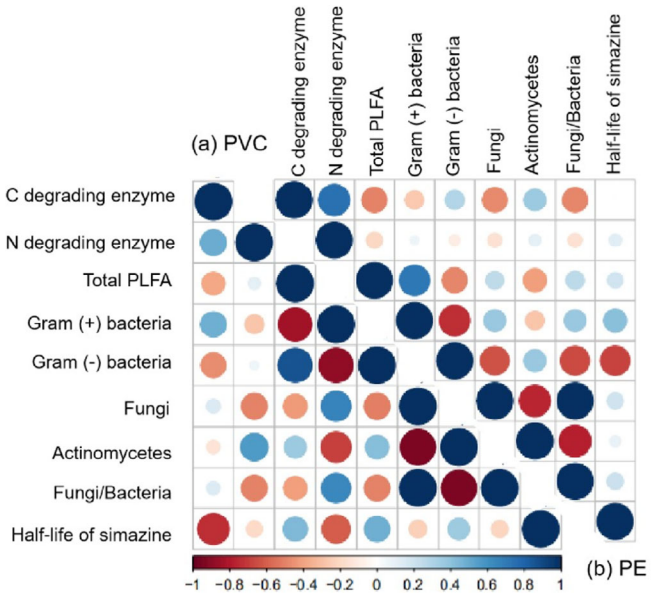

FIGURE 6 Correlation between C-degrading enzymes, N-degrading enzymes, total phospholipid fatty acid, gram (+) bacteria, gram (−) negative bacteria, fungi, Actinomycetes, the ratio of fungi and bacteria, as well as the half-life of simazine in soil added with polyvinyl chloride (a) and polyethylene (b) [Colour figure can be viewed at wileyonlinelibrary.com]

by the suppressed release of $^{14}CO_2$ from soil for both PVC (1%–20%, w/w) and PE (5%–20%, w/w) (Figure 1). Similarly, microplastic addition also increased the half-life of simazine by 0.5–1 day compared with the unamended Control treatment ($p < 0.05$, Figure 2). The observed reduction of herbicide mineralization may be explained by both direct and indirect influences of the presence of microplastics in soils. Directly, the herbicide may become sorbed to the surface of the plastic reducing its bioavailability (Holmes et al., 2012; Mato et al., 2001). For example, Ramos et al. (2015) found that PE film residues concentrated pesticides in soil. This sorption is then expected to reduce their potential to be lost to groundwater which could be seen as a positive attribute. Sorption processes are likely to be of particular significance for hydrophobic pesticides (e.g., K_{OW} >4). Simazine, however, is a hydrophilic compound ($K_{OW} = 2.18$) which is mobile in soil suggesting that it has a weak tendency to associate with plastic particles (Finizio et al., 1997). Similarly, Yang et al. (2018) found that microplastics cannot absorb the herbicide glyphosate and that it minimally interacts with plastics. This contrasts to biochar in soil which suppressed simazine degradation via sorption (Cheng et al., 2017). Therefore, the observed reduction in herbicide breakdown was not attributable to sorption but probably due to the influence of microplastics on soil microbial functioning.

After entering soil, microplastics can change the soil's physical structure, thus altering soil aggregation (Qi et al., 2020; Zhou, Wen, et al., 2021). Due to the low density (0.9–1.2 g cm^{-3}) of microplastics compared to soil (2.75 g cm^{-3}), however, microplastics will reduce soil bulk density. This is likely to affect root growth and also the activity and structure of the soil microbial community (Rillig et al., 2019). In

the same pot experiment, we observed that microplastics inhibited the growth of wheat (Zang et al., 2020). In turn, it could reduce rhizodeposition and as a consequence reduce the production of microbial enzymes due to a lack of energy resources (Wang et al., 2020; Zang et al., 2019). In line with this, PVC addition suppressed C-degrading enzymes, whilst 1% and 20% of PE addition decreased N-degrading enzymes, compared to the soil without microplastics ($p < 0.05$, Figure 4). Thus, a slowing down in C and/or N cycles in soils by decreased enzyme activities could also have suppressed herbicide degradation (i.e., hydrolases and esterases; Figure 7). This was also partly supported by a negative correlation between C-degrading enzymes and the half-life time of simazine in the soil amended with PVC ($r = 0.76$, $p < 0.05$, Figure 6). On the other hand, microplastics might have a direct toxic effect because of the presence of nonylphenol or other additive contaminants present within their matrix (Bokern & Harms, 1997; Hahladakis et al., 2018). It is accepted that microplastics can contaminate the surrounding soils (Hahladakis et al., 2018), thus potentially altering microbial growth and activity (Wang et al., 2016). In our case study, the addition of PVC (1% and 10%, w/w) and PE (1% and 20%, w/w) resulted in a shift in soil microbial community composition toward fungi, as indicated by a higher ratio of fungi-to-bacteria compared to the Control ($p < 0.05$, Figure 3). Given that bacteria can utilize and degrade a wide range of pollutants, that is, herbicides (Stroud et al., 2007), a shift from a bacterial to a fungal dominated microbial community by microplastics may affect herbicide degradation, thus increase the half-life time of simazine (Figure 7). This was corroborated with a negative correlation between Gram (+) bacteria and the half-life of simazine ($r = 0.54$, $p < 0.05$, Figure 6). Due to the significant correlation between C-degrading enzymes and bacteria in soil added with PVC, a shift from bacteria to fungi may also decrease the production of enzymes. Taken together, de Souza Machado et al. (2018) showed PE causes a higher water holding capacity in soil with greater moisture retention over time. Therefore, oxygen limitation may also inhibit native soil organic matter turnover (Keiluweit et al., 2016), and cause nutrient limitation for de novo enzyme production (Song et al., 2020). As a consequence, the shift in the microbial community structure and reduction in enzymes may cause an inhibition of simazine mineralization (Figure 7), which in turn, resulting in its accumulation and become toxic to non-target organisms.

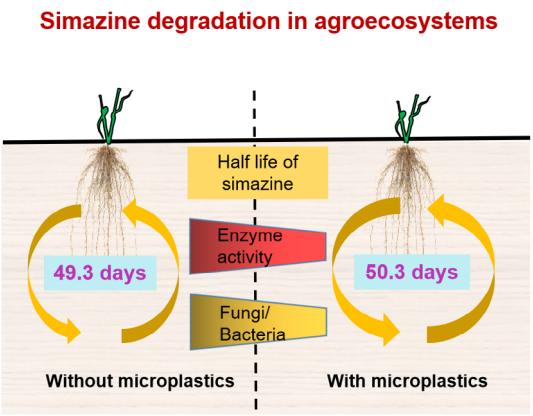

FIGURE 7 Schematic diagram of simazine decomposition in uncontaminated and microplastics contaminated agroecosystems. The microplastics used here were polyvinyl chloride and polyethylene at soil addition rates of 1%, 5%, 10%, and 20% by soil dry weight. The amount of simazine addition was based on the normal application of ~1.5 kg ha^{-1} and ~30% of which fell onto the soil surface. The grey value and yellow circles show the half-life of simazine in soil without and with microplastics pollution. The red and orange gradients between panels show the decreasing trend in fungi/bacterial ratio and enzyme activities between uncontaminated and microplastics contaminated soils [Colour figure can be viewed at wileyonlinelibrary.com]

It should also be noted that the effect of microplastics on the microbial community and enzyme activities are inconsistent, and did not show a linear relationship with the increased dose of microplastics. This may be because that the type and dose of microplastics as well as the interactions between these two factors played complex roles in the variations of the measured microbial functions (Figure 5). Given that PVC and PE had variable sorption capacities, which caused different surface-to-volume ratios of microplastics particles and subsequently provide specific microbial habitats (Brodhagen et al., 2017). This may explain the multiple effects of microplastics (i.e., PVC and PE) on microbial community structure and enzymes. Furthermore, we observed that the reduction in simazine decomposition rates was most acute at low additions of PVC rather than PE (Figure 2a). For example, the 1% (w/w) dose of PVC prolonged the simazine residues by 0.5 days compared to the Control ($p < 0.05$), whereas the half-life of simazine was not influenced by 1% (w/w) of PE ($p > 0.05$). PVC contains chlorine, which could cause stronger toxicity than PE, even under a lower dose of microplastics (Seeley et al., 2020; Zhou, Wen, et al., 2021). Therefore, PVC showed stronger inhibition of the enzyme activities and subsequent simazine degradation. As microplastics also possess no intrinsic microbial community or nutrients, at high concentrations they may also dilute the soil microbial community and available nutrient pool in soil, as a consequence higher dose of microplastics (5%–20%) did not show stronger effect on simazine compared to that under lower dose of microplastics (1%).

Given the reality that the majority of agricultural and urban soils are now contaminated by plastics, microplastic pollution may result in an accumulation of herbicide residues in soils, and become toxic to non-target organisms. In addition, herbicide residues in the soil may subsequently pollute groundwater through leaching (Silva et al., 2019), thereby affecting the quality of the agricultural crops and products. Both of these scenarios are likely to negatively affect public and ecosystem health (Singh et al., 2004). Therefore, it is essential to use environmentally friendly and sustainable approaches to either stimulate simazine mineralization or increase simazine sorption. For example, biochar application could be considered in the agricultural practices because of its' ability to immobilize herbicides and thus reduce the risk of herbicide leaching loss (Khalid et al., 2019).

5 | CONCLUSIONS

The effects of microplastics in agroecosystems remain largely unexplored although they are now widely acknowledged to have negative impacts in both freshwater and marine ecosystems. Our results indicated that even low levels of microplastic contamination will potentially decrease the short-term turnover of simazine, resulting in the accumulation of simazine residues in soil. We ascribe this to a microplastic-induced change in microbial community structure which leads to alterations in enzyme activity. This, in turn, may increase the risk of herbicides reaching surface waters (by runoff) or groundwater (by leaching) thereby impacting human health.

ACKNOWLEDGMENTS

This work was supported by the earmarked fund for China Agriculture Research System (CARS-07-B-5) and the UK Global Challenges Research Fund (GCRF) project awarded to Bangor University (NE/V005871/1). This work was supported by the UK-China Virtual Joint Centre for Agricultural Nitrogen (CINAg, BB/N013468/1), which is jointly supported by the Newton Fund, via UK Biotechnology and Biological Sciences Research Council and Natural Environment Research Council, and the Chinese Ministry of Science and Technology. Jie Zhou (201606850093) also would like to thank the China Scholarship Council (CSC) for funding to study in Germany.

CONFLICT OF 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.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Yuan Wen https://orcid.org/0000-0002-9612-7975
Hongguang Cheng https://orcid.org/0000-0003-4731-7374
Huadong Zang https://orcid.org/0000-0002-2008-143X

REFERENCES

Agnihotri, N. P., Vijay, P., Kumar, T., Mohapatra, M., & Salja, P. (1994). Organochlorine insecticide residues in Ganga River water near Farrukhabad, India. *Environmental Monitoring and Assessment*, *30*, 105–112. https://doi.org/10.1007/BF00545617

Arias-Estévez, M., Lòpez-Periago, E., Martìnez-Carballo, E., Simal-Gàndara, J., Mejuto, J. C., & Garcìa-Rìo, L. (2008). The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture, Ecosystems & Environment*, *123*, 247–260. https://doi.org/10.1016/j.agee.2007.07.011

Barber, J. A. S., & Parkin, C. S. (2003). Fluorescent tracer technique for measuring the quantity of pesticide deposited to soil following spray applications. *Crop Protection*, *22*, 15–21. https://doi.org/10.1016/S0261-2194(02)00061-3

Bartelt-Ryser, J., Joshi, J., Schmid, B., Brandl, H., & Balser, T. (2005). Soil feedbacks of plant diversity on soil microbial communities and subsequent plant growth. *Perspectives in Plant Ecology, Evolution and Systematics*, *7*, 27–49. https://doi.org/10.1016/j.ppees.2004.11.002

Bento, C. P. M., Yang, X. M., Gort, G., Xue, S., van Dam, R., Zomer, P., Mol, H. G. J., Ritsema, C. J., & Geissen, V. (2016). Persistence of glyphosate and aminomethylphosphonic acid in loess soil under different combinations of temperature, soil moisture and light/darkness. *Science of the Total Environment*, *572*, 301–311. https://doi.org/10.1016/j.scitotenv.2016.07.215

Boddy, E., Roberts, P., Hill, P. W., Farrar, J., & Jones, D. L. (2008). Turnover of low molecular weight dissolved organic C (DOC) and microbial C exhibit different temperature sensitivities in Arctic tundra soils. *Soil Biology and Biochemistry*, *40*, 1557–1566. https://doi.org/10.1016/j.soilbio.2008.01.030

Bokern, M., & Harms, H. H. (1997). Toxicity and metabolism of 4-n-nonylphenol in cell suspension cultures of different plant species. *Environmental Science & Technology*, *31*, 1849–1854. https://doi.org/10.1021/es960353r

Brodhagen, M., Goldberger, J. R., Hayes, D. G., Inglis, D. A., Marsh, T. L., & Miles, C. (2017). Policy considerations for limiting unintended residual plastic in agricultural soils. *Environmental Science & Policy*, *69*, 81–84. https://doi.org/10.1016/j.envsci.2016.12.014

Cheng, H., Jones, D. L., Hill, P., & Bastami, M. S. (2017). Biochar concomitantly increases simazine sorption in sandy loam soil and lowers its dissipation. *Archives of Agronomy and Soil Science*, *63*, 1082–1092. https://doi.org/10.1080/03650340.2016.1261117

de Souza Machado, A. A., Lau, C. W., Till, J., Kloas, W., Lehmann, A., Becker, R., & Rillig, M. C. (2018). Impacts of microplastics on the soil biophysical environment. *Environmental Science & Technology*, *52*, 9656–9665. https://doi.org/10.1021/acs.est.8b02212

FAO. (2014). *World reference base for soil resources 2014: International soil classification system for naming soils and creating legends for soil maps*. Rome: Food and Agriculture Organization of the United Nations.

Fenner, K., Canonica, S., Wackett, L. P., & Elsner, M. (2013). Evaluating pesticide degradation in the environment: Blind spots and emerging opportunities. *Science*, *341*, 752–758. https://doi.org/10.1126/science.1236281

Finizio, A., Vighi, M., & Sandroni, D. (1997). Determination of n-octanol/water partition coefficient (K_{ow}) of pesticide critical review and comparison of methods. *Chemosphere*, *34*, 131–161. https://doi.org/10.1016/S0045-6535(96)00355-4

Fuller, S., & Gautam, A. (2016). Procedure for measuring microplastics using pressurized fluid extraction. *Environmental Science & Technology*, *50*, 5774–5780. https://doi.org/10.1021/acs.est.6b00816

Glanville, H. C., Hill, P. W., Schnepf, A., Oburger, E., & Jones, D. L. (2016). Combined use of empirical data and mathematical modelling to better estimate the microbial turnover of isotopically labelled carbon substrates in soil. *Soil Biology and Biochemistry*, *94*, 154–168. https://doi.org/10.1016/j.soilbio.2015.11.016

Gong, W., Jiang, M., Han, P., Liang, G., Zhang, T. T., & Liu, G. N. (2019). Comparative analysis on the sorption kinetics and isotherms of fipronil on nondegradable and biodegradable microplastics. *Environmental Pollution*, *254*(112), 927. https://doi.org/10.1016/j.envpol.2019.07.095

Hahladakis, J. N., Velis, C. A., Weber, R., Iacovidou, E., & Purnell, P. (2018). An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. *Journal of Hazardous Materials*, *344*, 179–199. https://doi.org/10.1016/j.jhazmat.2017.10.014

Holmes, L. A., Turner, A., & Thompson, R. C. (2012). Adsorption of trace metals to plastic resin pellets in the marine environment. *Environmental Pollution*, *160*, 42–48. https://doi.org/10.1016/j.envpol.2011.08.052

Horton, A. A., Walton, A., Spurgeon, D. J., Lahive, E., & Svendsen, C. (2017). Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. *Science of the Total Environment*, *586*, 127–141. https://doi.org/10.1016/j.scitotenv.2017.01.190

Hüffer, T., Metzelder, F., Sigmund, G., Slawek, S., Schmidt, T., & Hofmann, T. (2019). Polyethylene microplastics influence the transport of organic contaminants in soil. *Science of the Total Environment*, *657*, 242–247. https://doi.org/10.1016/j.scitotenv.2018.12.047

Jiang, L. J., Imed, D., Hannah, M. M., Warren, A. D., & Doohan, D. (2011). The effect of straw mulch on simulated simazine leaching and runoff. *Weed Science*, *59*, 580–586. https://doi.org/10.1614/WS-D-10-00103.1

Jones, D. L., Edwards, J. G., & Murphy, D. (2011). Biochar mediated alterations in herbicide breakdown and leaching in soil. *Soil Biology and Biochemistry*, *43*, 804–813. https://doi.org/10.1016/j.soilbio.2010.12.015

Jones, D. L., Hill, P. W., Smith, A. R., Farrell, M., Ge, T., Banning, N. C., & Murphy, D. V. (2018). Role of substrate supply on microbial carbon use efficiency and its role in interpreting soil microbial community-level physiological profiles (CLPP). *Soil Biology and Biochemistry*, *123*, 1–6. https://doi.org/10.1016/j.soilbio.2018.04.014

Kasirajan, S., & Ngouajio, M. (2012). Polyethylene and biodegradable mulches for agricultural applications: A review. *Agronomy for Sustainable Development*, *32*, 501–529. http://doi.org/10.1007/s13593-012-0132-7

Keiluweit, M., Nico, P. S., Kleber, M., & Fendorf, S. (2016). Are oxygen limitations under recognized regulators of organic carbon turnover in upland soils? *Biogeochemistry*, *127*, 157–171. https://doi.org/10.1007/s10533-015-0180-6

Khalid, S., Shahid, M., Murtaza, B., Bibi, I., Naeem, M. A., & Niazi, N. K. (2019). A critical review of different factors governing the fate of pesticides in soil under biochar application. *Science of the Total Environment*, *134*, 645. https://doi.org/10.1016/j.scitotenv.2019.134645

Krutz, L. J., Burke, I. C., Reddy, K. N., Zablotowicz, R. M., & Price, A. J. (2009). Enhanced atrazine degradation: Evidence for reduced residual weed control and a method for identifying adapted soils and predicting herbicide persistence. *Weed Science*, *57*, 427–434. https://doi.org/10.1614/WS-09-010.1

Laabs, V., Amelung, W., Fent, G., Zech, W., & Kubiak, R. (2002). Fate of ^{14}C-labeled soybean and corn pesticides in tropical soils of Brazil under laboratory conditions. *Journal of Agricultural and Food Chemistry*, *50*, 4619–4627. https://doi.org/10.1021/jf0115443

Li, L., Zhang, Y., Zheng, L., Lu, S., Yan, Z., & Ling, J. (2018). Occurrence, distribution and ecological risk assessment of the herbicide simazine: A case study. *Chemosphere*, *204*, 442–449. https://doi.org/10.1016/j.chemosphere.2018.04.009

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., & Kaminuma, T. (2001). Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environmental Science & Technology*, *35*, 318–324. https://doi.org/10.1021/es0010498

Ng, E. L., Huerta Lwanga, E., Eldridge, S. M., Johnston, P., Hu, H. W., Geissen, V., & Chen, D. L. (2018). An overview of microplastic and nanoplastic pollution in agroecosystems. *Science of the Total Environment*, *627*, 1377–1388. https://doi.org/10.1016/j.scitotenv.2018.01.341

PPDB, 2015. The Pesticide Properties Database (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire, funded by UK national sources and the EU-funded FOOTPRINT project (FP6-SSP-022704). Available from: http://sitem.herts.ac.uk/aeru/projects/ppdb/

Qi, R., Jones, D. L., Li, Z., Liu, Q., & Yan, C. (2020). Behavior of microplastics and plastic film residues in the soil environment: A critical review. *Science of the Total Environment*, *703*(134), 722. https://doi.org/10.1016/j.scitotenv.2019.134722

Ramos, L., Berenstein, G., Hughes, E. A., Zalts, A., & Montserrat, J. M. (2015). Polyethylene film incorporation into the horticultural soil of small periurban production units in Argentina. *Science of the Total Environment*, *523*, 74–81. https://doi.org/10.1016/j.scitotenv.2015.03.142

Rillig, M. C., Lehmann, A., de Souza Machado, A. A., & Yang, G. (2019). Microplastic effects on plants. *New Phytologist*, *223*, 1066–1070. https://doi.org/10.1111/nph.15794

Seeger, M., Hernández, M., Méndez, V., Ponce, B., Córdova, M., & González, M. (2010). Bacterial degradation and bioremediation of chlorinated herbicides and biphenyls. *Journal of Soil Science and Plant Nutrition*, *10*, 320–332. http://doi.org/10.4067/S0718-95162010000100007

Seeley, M. E., Song, B., Passie, R., & Hale, R. C. (2020). Microplastics affect sedimentary microbial communities and nitrogen cycling. *Nature Communications*, *11*, 2372. https://doi.org/10.1038/s41467-020-16235-3

Silva, V., Mol, H. G. J., Zomer, P., Tienstra, M., Ritsema, C. J., & Geissen, V. (2019). Pesticide residues in European agricultural soils - a hidden reality unfolded. *Science of the Total Environment*, *653*, 1532–1545. https://doi.org/10.1016/j.scitotenv.2018.10.441

Singh, K. P., Mohan, D., Sinha, S., & Dalwani, S. (2004). Impact assessment of treated/untreated wastewaters toxicants discharged by sewage treatment plants on health, agricultural and environmental quality in the waste water disposal area. *Chemosphere*, *55*, 227–255. https://doi.org/10.1016/j.chemosphere.2003.10.050

Song, X., Razavi, B., Ludwig, B., Zamanian, K., Zang, H., Kuzyakov, Y., Dippold, M., & Gunina, A. (2020). Combined biochar and nitrogen application stimulates enzyme activity and root plasticity. *Science of the Total Environment*, *735*(139), 393. https://doi.org/10.1016/j.scitotenv.2020.139393

Steinmetz, Z., Wollmann, C., Schaefer, M., Buchmann, C., David, J., Troger, J., Munoz, K., Fror, O., & Schaumann, G. E. (2016). Plastic mulching in agriculture. Trading short-term agronomic benefits for -term soil degradation? *Science of the Total Environment*, *550*, 690–705. https://doi.org/10.1016/j.scitotenv.2016.01.153

Stroud, J. L., Paton, G. I., & Semple, K. T. (2007). Microbe-aliphatic hydrocarbon interactions in soil: Implications for biodegradation and bioremediation. *Journal of Applied Microbiology*, *102*, 1239–1253. https://doi.org/10.1111/j.1365-2672.2007.03401.x

Toccalino, P. L., Gilliom, R. J., Lindsey, B. D., & Rupert, M. G. (2014). Pesticides in groundwater of the United States: Decadal-scale changes, 1993–2011. *Ground Water*, *52*, 112–125. https://doi.org/10.1111/gwat.12176

Vox, G., Loisi, R. V., Blanco, I., Mugnozza, G. S., & Schettini, E. (2016). Mapping of agriculture plastic waste. *Agriculture and Agricultural Science Procedia*, *8*, 583–591. https://doi.org/10.1016/j.aaspro.2016.02.080

Wang, J., Lv, S., Zhang, M., Chen, G., Zhu, T., Zhang, S., Teng, Y., Christie, P., & Luo, Y. (2016). Effects of plastic film residues on occurrence of phthalates and microbial activity in soils. *Chemosphere*, *151*, 171–177. https://doi.org/10.1016/j.chemosphere.2016.02.076

Wang, X., Yang, Y. D., Pei, K., Zhou, J., Peixoto, L., Gunina, A., Zeng, Z., Zang, H., Rasmussen, J., & Kuzyakov, Y. (2020). Nitrogen rhizodeposition of legumes and its fate in agroecosystems: Field study and literature review. *Land Degradation & Development*, *32*, 410–419. https://doi.org/10.1002/ldr.3729

Wen, Y., Zang, H., Freeman, B., Musarika, S., Evans, C., Chadwick, D., & Jones, D. (2019). Microbial utilization of low molecular weight organic carbon substrates in cultivated peats in response to warming and soil degradation. *Soil Biology and Biochemistry*, *139*, 629. 107629. https://doi.org/10.1016/j.soilbio.2019.107629

Wen, Y., Zang, H., Ma, Q., Evans, C. D., Chadwick, D. R., & Jones, D. L. (2019). Is the 'enzyme latch' or 'iron gate' the key to protecting soil organic carbon in peatlands? *Geoderma*, *349*, 107–113. https://doi.org/10.1016/j.geoderma.2019.04.023

Yang, X., Bento, C. P. M., Chen, H., Zhang, H., Xue, S., Lwanga, E. H., Zomer, P., Ritsema, C. J., & Geissen, V. (2018). Influence of microplastic addition on glyphosate decay and soil microbial activities in Chinese loess soil. *Environmental Pollution*, *242*, 338–347. https://doi.org/10.1016/j.envpol.2018.07.006

Zang, H., Xiao, M., Wang, Y., Ling, N., Wu, J., Ge, T., & Kuzyakov, Y. (2019). Allocation of assimilated carbon in paddies depending on rice age, chase period and N fertilization: Experiment with $^{13}CO_2$ labelling and literature synthesis. *Plant and Soil*, *445*, 113–123. https://doi.org/10.1007/s11104-019-03995-1

Zang, H., Zhou, J., Marshall, M. R., Chadwick, D. R., Wen, Y., & Jones, D. L. (2020). Microplastics in the agroecosystem: Are they an emerging threat to the plant-soil system? *Soil Biology and Biochemistry*, *148*, 107926. https://doi.org/10.1016/j.soilbio.2020.107926

Zhou, J., Gui, H., Banfield, C. C., Wen, Y., Zang, H. D., Dippold, M. A., Charlton, A., & Jones, D. L. (2021). The microplastisphere: Biodegradable microplastics addition alters soil microbial community structure and function. *Soil Biology and Biochemistry*, *156*, 108211. https://doi.org/10.1016/j.soilbio.2021.108211

Zhou, J., Wen, Y., Marshall, M. R., Zhao, J., Gui, H., Zeng, Z. H., Jones, D. L., & Zang, H. D. (2021). Microplastics as an emerging threat to plant and soil health in agroecosystems. *Science of the Total Environment*, *787*, 147444. https://doi.org/10.1016/j.scitotenv.2021.147444

Zhou, J., Zang, H., Loeppmann, S., Gube, M., Kuzyakov, Y., & Pausch, J. (2020). Arbuscular mycorrhiza enhances rhizodeposition and reduces the rhizosphere priming effect on the decomposition of soil organic matter. *Soil Biology and Biochemistry*, *140*, 107641. https://doi.org/10.1016/j.soilbio.2019.107641

How to cite this article: Zhou, J., Wen, Y., Cheng, H., Zang, H., & Jones, D. L. (2022). Simazine degradation in agroecosystems: Will it be affected by the type and amount of microplastic pollution? *Land Degradation & Development*, *33*(7), 1128–1136. https://doi.org/10.1002/ldr.4243